T H E S I S .

(1) THE DIALKYLPHENYLAMINES: THEIR PREPARATION AND OXIDATION.

(2) THE CONDENSATION OF FLUORENE AND ACETONE.

BY

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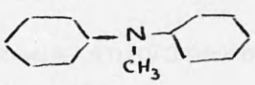
A L K Y L - D I P H E N Y L A M I N E S :

THEIR PREPARATION AND OXIDATION.

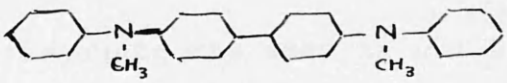
ALKYL-DIPHENYLAMINES: THEIR PREPARATION AND OXIDATION.

INTRODUCTION.

Oxidation in the carbazole series had led to the production of various dicarbazyls (i); a similar oxidation of N-methyldiphenylamine had produced N:N'-dimethyl-N:N'-diphenyl benzidine:-



N-methyldiphenylamine



N:N'dimethyl-N:N'-diphenyl-benzidine.

N-Ethyldiphenylamine did not react similarly as it yielded N-acetyldiphenylamine instead of the expected N:N'-ethyl-N:N'-diphenylbenzidine, therefore investigations were then undertaken with other N-alkyldiphenylamines and derivatives of N-ethyldiphenylamine.

As no other method yielded any isolatable product from N-ethyldiphenylamine, the original oxidising agent, potassium permanganate in acetone, was adhered to with all other N-alkyl diphenylamines.

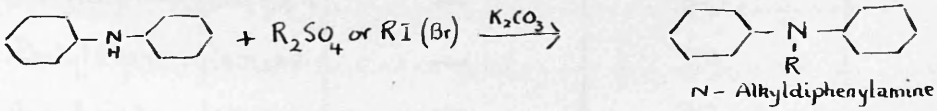
The best method of preparation of each of the various N-alkyldiphenylamines required for the research was evolved, and comparison made, where possible, with existing preparations described in the literature.

THE PREPARATION OF N-ALKYLDIPHENYLAMINES.

The preparation of N-Alkyldiphenylamines (ii) was accomplished by three methods: Alkylation by the di-alkylsulphates (iii,iv, v,), by alkyl iodides (vi), and bromides, of both diphenylamine and diphenylamine magnesium bromide.

It was intended to discover the best method of preparation of each individual amine and also that showing the most general application.

Excess anhydrous potassium carbonate was used in all alkylations, other than those of diphenylamine magnesium bromide, to remove acid by-products.



N - Alkyldiphenylamine.

The production of N-alkyldiphenylamines by the action of di-alkyl sulphates on diphenylamine was satisfactory with two lowest members of the series only; with the longer alkyl chains a sharp drop in yields and increasing inavailability of the sulphates rendered the method impracticable.

Alkyl iodides showed greater general practicability although the yields decreased with increase of molecular weight of the alkyl group. Spatial configuration of the group had little or no influence on the yield. This was in direct contrast to the work of Skita, Keil, and Haverman (ii) who found that, by their method of preparation, branched alkyl chains gave much poorer results.

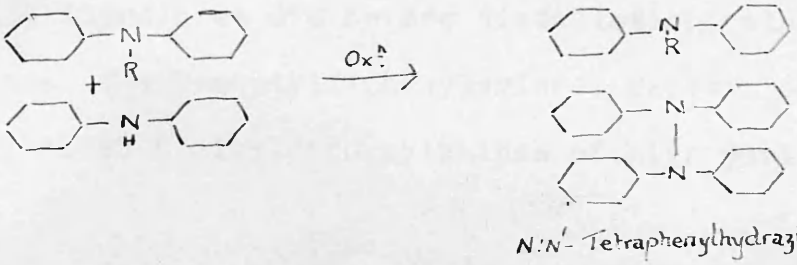
Alkyl bromides were of little value, and alkylations of diphenylamine magnesium bromide were successful with N-ethyldiphenylamine only.

The results are tabulated below:-

Amine.	% Yields on Alkylation by.....		
	Dialkyl sulphates.	Alkyl Iodides.	Alkyl Bromides.
N- Methyldiphenylamine	85	40	—
N- Ethyldiphenylamine	80	80	0.
N-n-Propyldiphenylamine	40	50	2.
N-iso-Propyldiphenylamine	—	50	2.
N-n-Butyldiphenylamine	—	40	30.
N-iso-Butyldiphenylamine	—	33	—
N-n-Amyldiphenylamine	—	30.	—
N-β-Phenethyldiphenylamine	—	—	45.
N- Benzyldiphenylamine	{From $\phi.CH_2Cl$}		90%- 95%

The complete separation of the tertiary amine from unchanged diphenylamine caused difficulty. Three methods were used:

(a) The oxidation of unchanged diphenylamine to tetraphenylhydrazine, then distillation of the tertiary amine from the mixture:-



N:N'- Tetraphenylhydrazine.

(b) Extraction of tertiary amine with cold concentrated hydrochloric acid which simultaneously precipitated diphenylamine hydrochloride.

(c) Acetylation of the diphenylamine in the mixture followed by the separation of the N-alkyldiphenylamine from the N-acetyldiphenylamine produced by (1) direct distillation, (2) extraction at 0°C with ligroin in which the N-acetyldiphenylamine was practically insoluble.

Only one of these methods (c2) gave satisfactory results. Separation by (a) partially decomposed the tertiary amine and had to be repeated because of incomplete oxidation of the diphenylamine. Method (b) had a limited application as N-n-propyl diphenylamine was sparingly soluble, and the higher N-alkyldiphenylamines practically insoluble in concentrated hydrochloric acid. (c) Acetylation by acetic anhydride (ii) removed the diphenylamine completely, but, especially with the larger alkyl chains, decomposed some of the tertiary amine. A method was evolved using acetyl chloride in the presence of sodium acetate, which was as efficient as the former, yet did not affet the tertiary amine. Separation of N-alkyldiphenylamine from N-acetyldiphenylamine by fractional distillation in vacuo as described in (ii), was not absolute, especially with the higher boiling N-alkyldiphenylamines. Extraction of the mixture, however, with ligroin at 0°C before distillation, almost completely precipitated the N-acetyldiphenylamine. Repetition of this process yielded N-alkyldiphenylamines of high purity.

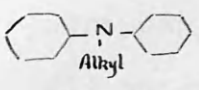
The purity of a sample was tested by bromination in glacial acetic acid: if diphenylamine was present the solution assumed a blue colour on standing, and if N-acetyldiphenylamine was present a very insoluble product was formed. N-alkyldiphenylamines obtained by method (c2) gave negative results to these tests.

A colour test for N-alkyldiphenylamines has been discovered: One or two drops of concentrated nitric acid then a few ccs. of water were added to minute traces of N-alkyldiphenylamine. The solution assumed a permanent crimson colour characteristic of N-alkyldiphenylamines.

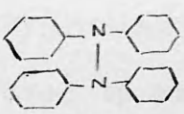
N.B. Diphenylamine did not exhibit a like reaction as the original purple colour developed rapidly changed to black followed by precipitation of the solution.

THE OXIDATION OF N-ALKYLDIPHENYLAMINES.

The N-Alkyldiphenylamines (I) were oxidised by potassium permanganate in acetone in the presence of sodium bicarbonate to give N-N'-tetraphenylhydrazine (II). Four exceptions to this rule were noted: N-methyldiphenylamine yielded N-N'-dimethyl-N:N'-diphenylbenzidine (III), N-ethyl- and N-benzyl diphenylamines the corresponding N-acyldiphenylamines (IV) respectively, while N-β-phenethyldiphenylamine (V) was unaffected by the oxidising agent.



(I)



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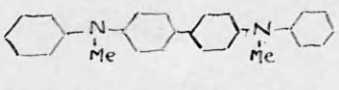

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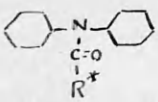
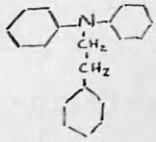


(IV)



(V)

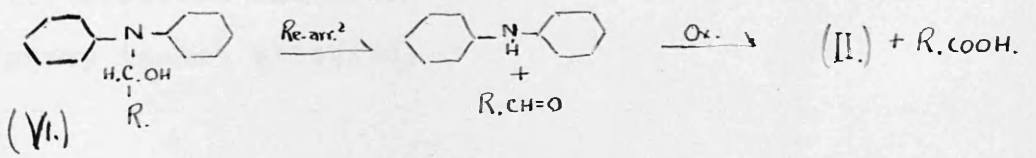
* R = Me, Phenyl.

The yields of N-acetyldiphenylamine or N:N'-tetraphenylhydrazine obtained by these oxidations were poor- 10%-15% in all but one case, that of N-benzoyldiphenylamine (70%).

Of further interest was the curious observation that derivatives of N-ethyldiphenylamine oxidised to the corresponding N-acyldiphenylamine, but derivatives of the N-alkyldiphenylamines which oxidised to N:N'-tetraphenylhydrazine were apparently unaffected by the reagent.

The mechanism of the reaction has not been definitely determined. Apparently a N-α-hydroxyalkyldiphenylamine (VI) is formed intermediately and rearranges almost instantaneously to one molecule of diphenylamine and one molecule of the corresponding aldehyde. The diphenylamine formed is oxidised to N:N'-tetraphenylhydrazine and the aldehyde to the acid.

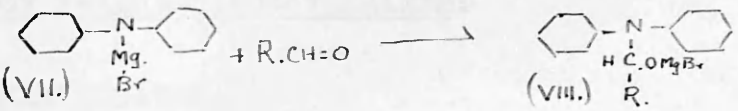
N.B. As in the preparation of N:N'-tetraphenylhydrazine from diphenylamine the oxidation is carried out at 0°C; this may partly account for the low yields obtained.



The N-acyldiphenylamines were found to be stable to the oxidising agent, therefore the possibility that (VI) was primarily oxidised to an N-acyldiphenylamine and subsequently produced N:N'-tetraphenylhydrazine is untenable.

(VI) has proved to be very unstable (and probably non-existent

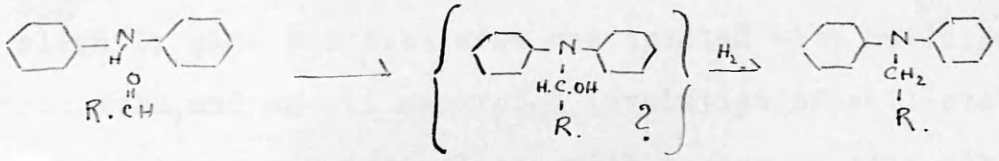
as a free base) by the preparation of the magnesium bromide salts (VIII) from diphenylamine-N-magnesium bromide (VII) and an aldehyde.



(VII.) (VIII.)

All attempts to free the base from the salt (VIII) regenerated the aldehyde and diphenylamine.

Some support to the possibility of the intermediate formation of an N-α-hydroxyalkyldiphenylamine has been noted in a 'converse' manner in the preparation of N-alkyldiphenylamines (ii) from diphenylamine, an aldehyde, and hydrogen under pressure.



We can only assume, due to lack of evidence, that the α-hydroxy-amines formed from N-ethyl- and N-benzyl diphenylamines are preferentially oxidised.

In the reported oxidation of N-methyl diphenylamine the N-alkyl group is not attacked.

EXPERIMENTAL.

PREPARATION OF N-ALKYLDIPHENYLAMINES:

(A) BY DIALKYLSULPHATES.

Diphenylamine (95 g.), diethyl sulphate (95 g., 2 mols.) and excess anhydrous potassium carbonate (100 g.) were thoroughly shaken (till the mass became fluid) in a flask fitted with a short air reflux then water condenser in a distillation position, and heated at 175°-180°C for three hours.

A distillate of alcohol and water is obtained.

The slightly pink reaction mass was treated with hot dilute hydrochloric acid, and an oil separated (evolution of evil-smelling vapours). The liquor was neutralised with excess caustic alkali, the oil extracted with ligroin, and the extract washed, dried, and fractionally distilled in vacuo, the fraction b.p. 150°-170°/15 mm being retained.

Purification of this crude N-ethyldiphenylamine was accomplished thus:-

The fraction was mixed with fused sodium acetate (95 g.). (Flask and reflux condenser). Acetyl chloride (87 g.) was added in four parts, the mixture being vigorously ~~should be~~ was shaken after each addition. (The mixture, should it turn green, ~~should be~~ was shaken till an orange colour re-developed.) Much heat was evolved.

The mixture was poured into water, boiled for five minutes,

and when cool, extracted with ligroin (60°-80°C). The solution was filtered from the crystals of N-acetyldiphenylamine precipitated, and the ligroin extract washed and dried for twenty-four hours at 0°C to precipitate the remaining N-acetyldiphenylamine. Fractional distillation in vacuo yielded 80%-85% of theoretical of pure N-ethyldiphenylamine b.p. 152°-155°/12 mm.

N.B. For subsequent %age yields see page 3 .

Similarly N-n-propyldiphenylamine was prepared.

(B) BY DIALKYLSULPHATE ON DIPHENYLAMINE MAGNESIUM BROMIDE.

To diphenylamine magnesium bromide (1 mol.), suspended in ether, was added slowly diethyl sulphate (2 mols.) in ether. The mixture was then boiled for one hour, then treated with dilute sulphuric acid. The N-ethyldiphenylamine produced was isolated and purified as in (A).

(C) BY ALKYL IODIDES OR BROMIDES.

Diphenylamine (1 mol.), alkyl iodide (or bromide) (1.5 mol), and anhydrous potassium carbonate (1.5 mol.), were boiled (at the boiling point of the alkyl halide) for forty-eight hours. The N-alkyldiphenylamine was isolated and purified as in (A).

The various N-alkyldiphenylamines so prepared were:-

(1) By alkyl iodides - N-methyl-, N-ethyl-, N-n-propyl-, N-n-butyl-, N-iso-butyl-, N-iso-propyl-*, N-n-amyl-**, diphenylamines. (2) By alkylbromides - N-n-propyl and N-n-butyl diphenylamines.

*B.P.155°/12mm $C_{15}H_{17}N$ req. C,85.3%;H,8.0%. Found C,85.2%;H,7.8%.

**B.P.190°/12mm $C_{17}H_{21}N$ req.C,85.35%;H,8.8%. Found C,85.3%;H,8.6%.

N-Benzyldiphenylamine.

Benzyl chloride (30 g.,1.2 mols.), diphenylamine (34g. 1 mol.), and anhydrous potassium carbonate (35 g.) were heared at 200°C for two hours. The reaction mass was steam-distilled to remove unchanged benzyl chloride (or alcohol), the residue was extracted with ligroin (60°-80°). The residue, on distillation of the ligroin, was crystallised from alcohol. M.P. 86°C. Yield: 44g.; c'a 90%.

N-β-Phenethyldiphenylamine.

β-Phenethyl ~~chloride~~ bromide (1.5 mols.), diphenylamine (1 mol.) and anhydrous potassium carbonate (excess) were heated at 150°C for forty-eight hours. The tertiary amine was isolated and purified as under (A~~)~~.

M.P. 61°C; B.P. 220°C/11 mm. Yield: C'a 50%.

$C_{20}H_{19}N$ requires: C,87.9%; H,6.95%; N,5.15%.

Found: C,87.9%; H,6.8%; N,5.09%.

4:4'-Dibromo-N-iso-propyldiphenylamine.

N-iso-Propyldiphenylamine (5 grm.) in glacial acetic acid (40 cc.) was mechanically stirred, while bromine (7.6g.) in acetic acid (20 cc) was slowly added. When hydrobromic

acid ceased to be evolved the white crystalline solid was filtered and crystallised from alcohol. M.P. 92°C. Dilution of the acetic acid with water precipitated more of the substance. Yield: 8.5 g.; c'a 100%.

$C_{15}H_{15}NBr_2$ requires: C,48.7%; H,4.1%.

Found: C,48.83%;H,4.38%.

The dibromo derivatives of N-ethyl-, N-n-propyl-, N-n-butyl- diphenylamines were similarly prepared.

OXIDATION OF N-ETHYLDIPHENYLAMINE.

N-Ethyldiphenylamine (1 g.), potassium permanganate (1 g.), sodium bicarbonate (1 g.) in acetone (20 cc) were boiled for one hour, then the contents were poured into sulphurous acid solution. The oily aqueous liquid was extracted overnight at 0°C with ligroin (60°-80°). The N-acetyldiphenylamine, precipitated at the intersurface of the liquids was recrystallised from ligroin.

Yield never over 15%.

Similarly N-benzyldiphenylamine yielded N-benzoyl-diphenylamine (70%).

2-Nitro-N-ethyldiphenylamine and 4:4'-dibromo-

-N-ethyldiphenylamine yielded traces of 2-nitro-N-acetyl-, and 4:4'-dibromo-N-acetyl- diphenylamines respectively. In the former case the ligroin extract was allowed to evaporate to dryness and the crystals hand-picked, while in the case of the dibromodiphenylamine the product was obtained by repeated crystallisation from alcohol.

OXIDATION OF N-n-PROPYLDIPHENYLAMINE.

N-n-Propyldiphenylamine (1 g.), potassium permanganate (1 g.), sodium bicarbonate (1 g.), in acetone (20 cc), were boiled for one hour then treated as in the oxidation of N-ethyldiphenylamine. The yields of N:N'-tetraphenylhydrazine precipitated at the interface of the ligroin and water; never exceeded 15%.

Similarly N-n-butyl-, N-n-amyl-, N-iso-propyl-, and N-iso-butyl- diphenylamines yielded like quantities of N:N'-tetraphenylhydrazine.

After similar treatment 4:4'-dibromo-N-n-propyldiphenylamine, N-acyldiphenylamines, and N-β-Phenethyldiphenylamine, were recovered unchanged from the reaction.

DIPHENYLAMINE-N-MAGNESIUM BROMIDE.

Diphenylamine (10 g.) in dry ether (60 cc) was added slowly with mechanical stirring to a solution of ethyl magnesium bromide (c'a 8 g.) in ether (40 cc) in an inert atmosphere. A vigorous evolution of ethane was noted and heat was evolved.

When all the diphenylamine had been added the solution suddenly deposited white diphenylamine magnesium bromide. (Care, rush of gas due to heat of precipitation.)

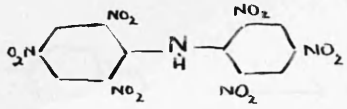
REACTION OF AN ALDEHYDE ON DIPHENYLAMINE MAGNESIUM BROMIDE.

An aldehyde (1.05 mols.) in dry ether, was added in an inert atmosphere to diphenylamine magnesium bromide (1 mol.) in ether. On boiling for two hours the colour of the insoluble material changed to light brown. Filtration and washing with dry ether yielded abrown amorphous powder, which on treatment with water, dilute acid or alkali, decomposed into diphenylamine and the aldehyde.

NOTE:

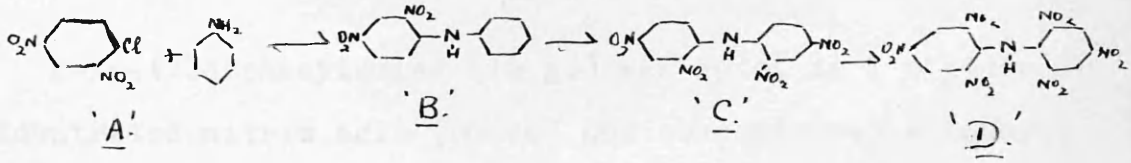
ON A NEW METHOD FOR THE PREPARATION OF DIPICRYLAMINE.

(2:4:6:2':4':6'-HEXANITRODIPHENYLAMINE.)



Dipicrylamine is a violently explosive substance, and found considerable application in the great war (1914-1918) as a 'booster' for the T.N.T. in torpedoes.

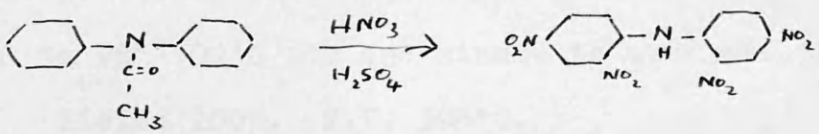
Various methods of preparation have been described.(vii) As the yield of dipicrylamine by direct nitration of diphenylamine (viii) was poor , the following reactions (A-D) were carried out in industry in order to obtain the explosive in quantity:



'A' 'B' 'C' 'D'

(The various stages require no explanation.)

It was found, however, that when N-acetyldiphenylamine was nitrated under carefully regulated conditions a theoretical yield of 2:4:2':4'-tetranitrodiphenylamine was obtained.



This substance was dissolved in fuming nitric acid (d 1.5 and concentrated sulphuric acid was added slowly to the solution, which precipitated dipicrylamine. (95% yield.)

Dipicrylamine.

The only previous reference to any nitration of N-acetyldiphenylamine was in 1903 when 2:4:2':4'-tetranitrodiphenylamine was obtained with other products on nitration by diacetyl-ortho-nitric acid. (ix).

EXPERIMENTAL.

2:4:2':4'-Tetranitrodiphenylamine.

N-Acetyldiphenylamine (12 g.) was added to a mixture of concentrated nitric acid (50 cc) and concentrated sulphuric acid (25 cc) at 15°C. On stirring the amine dissolved and the solution assumed a greenish colour; the temperature of the solution rose spontaneously to 65°C, during which time the colour of the solution had changed through brown, orange, to a dark red at that temperature. The temperature of the mixture was then gently raised to 70°-75°C when a crystalline yellow precipitate appeared. After 5-10 minutes the solution was heated to 95°-100°C for one minute to complete the reaction. Yield: 100%. M.P. 198°C.

Dipicrylamine.

The tetranitrodiphenylamine prepared as before was dissolved in a minimum of fuming nitric acid (d 1.5). Addition of concentrated sulphuric acid to this solution precipitated dipicrylamine. (Exothermic reaction.)

Yield: 95%. M.P. 238°C.

N.B. A sample of the liquors from the above should be tested with more concentrated sulphuric acid to ensure complete precipitation.

I N D E X .

(i) Maitland and Tucker: J.C.S. 1927, 1388-92.

(ii)Skita, Keil, and Havemann: Ber. 66 B, 1400-11;
Girard: Bull. Soc., 23 (2), 3.

(iii)Gibson and Vining: J.C.S. 1923, 831-841.

(iv)Ullmann: Ann. 327, 113.

(v) Wieland: Ber. 52, 890.

(vi)Bardz: Zeit. für angew. Chem. 1871, 469.

(vii)Refer to Beistein, Bd XII, 766,and Additional Bd.XII,369.

(viii)Gnehm: Ber. 7, 1399.

(ix)Pictet: Compt. Rend., 1903 II, 1109.

THE

CONDENSATION OF FLUORENE

WITH ACETONE.

THE CONDENSATION OF FLUORENE AND ACETONE.

CONTENTS.

The following research, although entitled: "Condensation of Fluorene with Acetone", is essentially the "Elucidation of the Structures, Syntheses, and general Chemistry of the Substances derived from the Product of Condensation".

As these substances have proved to be derivatives of the hydrocarbon Fluoranthene, a short summary of the Chemistry of that substance, derived from miscellaneous reports in the Chemical Literature has been included as a foreword.

PART I.

F L U O R A N T H E N E .

A SHORT SUMMARY OF ITS HISTORY AND CHEMISTRY.

C O N T E N T S .

I N T R O D U C T I O N .

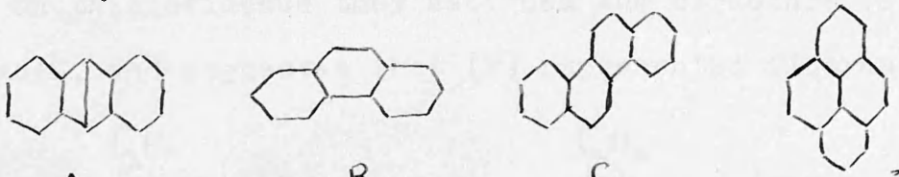
The hydrocarbon fluoranthene, although it has been known for over sixty years, has been little investigated. Indeed, the true chemical structure of the substance was determined only about twelve years ago, and this, together with the great difficulties in isolation encountered earlier, have left the Chemistry of the hydrocarbon little beyond the preliminary stages.

As far as has been determined, no general survey of the Chemistry of fluoranthene has yet been published; thus, in view of the developement of the research reported in this thesis, it has been considered advantageous to collect the previous work done on the hydrocarbon, in order to present this work in the light of existing knowledge.

II. THE DISCOVERY OF FLUORANTHENE AND THE ELUCIDATION OF ITS STRUCTURE; SYNTHESES.

The credit for the original discovery of fluoranthene (or idryl as it was often called) was the subject of considerable dispute. In 1878, two authors, Goldschmidt (i) and Fittig and Gebhard (ii) independently isolated the hydrocarbon from different sources.

Goldschmidt discovered a new hydrocarbon, m.p. 110°C, along with the known hydrocarbons anthracene (A), phenanthrene (B), chrysene (C), and pyrene(D), which he isolated from the 'Stupp' fat residues remaining after distillation of mercury from the ores at Idria.



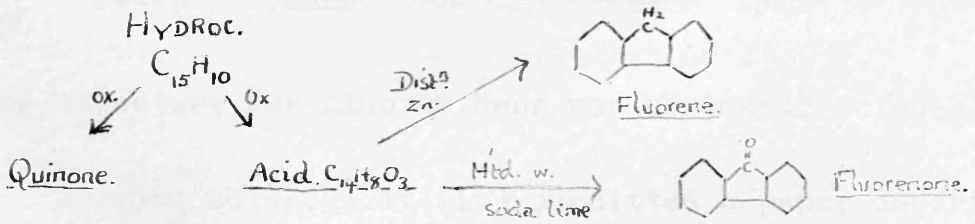
A. B. C. D.

To this new hydrocarbon he gave the name 'Idryl'. His preliminary investigations into the structure discovered the fact that oxidation of Idryl produced an acid, and a quinone, which yielded diphenyl on heating with soda-lime. On vapour-density and analytical determinations he allocated the empirical formula $C_{15}H_{10}$ to the hydrocarbon.

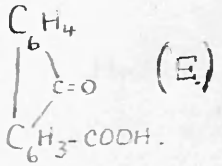
Fittig and Gebhard, about one month later, succeeded in isolating a hydrocarbon, m.p. 109°C, from coal tar

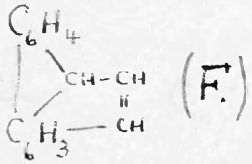
distillate boiling at over 360°C. This hydrocarbon, they alleged was identical with Goldschmidt's 'Idryl'.

Chemical investigations by these authors gave more definite evidence of structure. They found that the acid obtained similarly to that acid reported by Goldschmidt, had an empirical formula $C_{14}H_8O_3$, yielded fluorenone on heating with soda-lime, and fluorene on distillation with zinc dust:



On this evidence they assigned the structure (E) to the acid, and suggested that (F) represented fluoranthene.

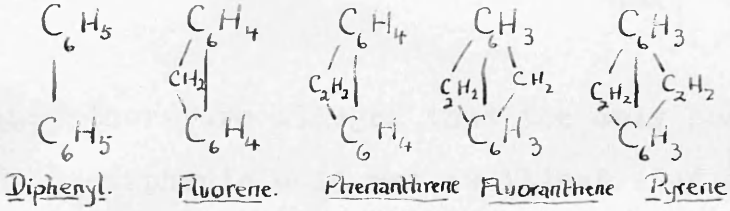




Because of the relative similarit y of relationship between the hydrocarbon and fluorene, to that between phenanthrene and diphenyl, Fittig and Gebhard allocated the name fluoranthene to the hydrocarbon.

(Both names, idryl and fluoranthene are found in the Chemical Literature till about 1910, since then the name idryl has been dropped in favour of fluoranthene.)

At this time, 1879, because of the erroneous empirical formula $C_{15}H_{10}$, fluoranthene was apparently considered an 'intermediate' between phenanthrene $C_{14}H_{10}$ and pyrene $C_{16}H_{10}$. Atterberg (iii) was the only author to suggest intermediate structural relationships between the substances:



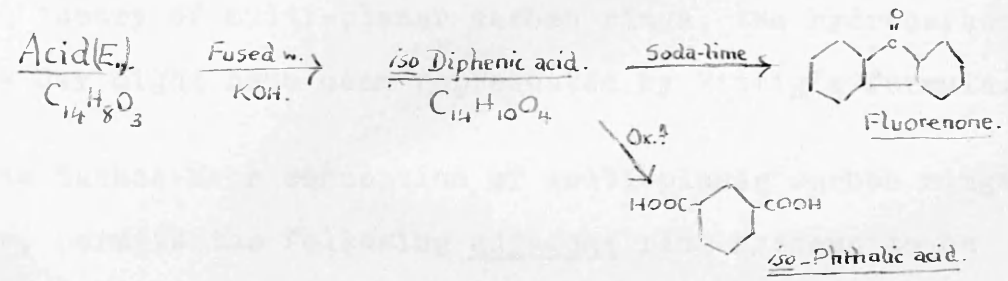
This structure for fluoranthene was obviously untenable.

In 1880 Goldschmidt (iv) submitted a paper describing several simple derivatives of fluoranthene, the most important of which was the apparent production of a dihydrofluoranthene, $C_{15}H_{12}$, by the restricted action of hydriodic acid and phosphorus.

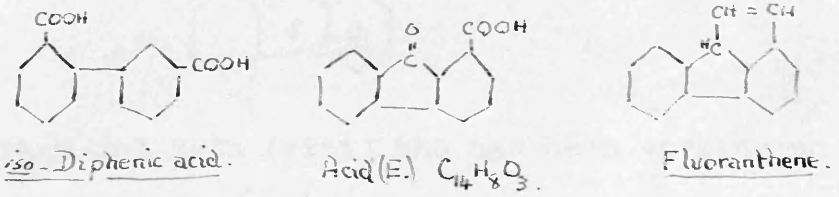
Hydroc. Fluoranthene $C_{15}H_{10}$ $\xrightarrow{H_2}$ $C_{15}H_{12}$ (?)

In the same year important evidence regarding the structure of fluoranthene was furnished by Fittig and Gebhard (v), who discovered that the acid (E) obtained by the oxidation of fluoranthene yielded an unknown diphenic acid, which they called <u>iso</u>diphenic acid, on fusion with potash. Fittig and Lippman (vi) furthermore found that this <u>iso</u>diphenic acid gave <u>iso</u>phthalic acid on oxidation. Yet this <u>iso</u>diphenic acid yielded fluorenone when heated with soda-lime, thereby

proving that one of the carboxyl groups was 'ortho' to the diphenyl linkage.

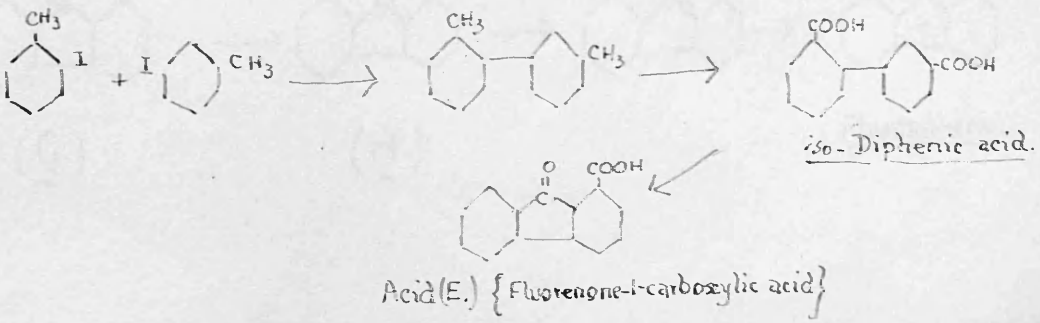


They therefore alleged that the only possible structure for the isodiphenic acid was as illustrated ~~above~~ below, and, as a corollary, that the acid (E) $C_{14}H_8O_3$, obtained by oxidising fluoranthene, and similarly fluoranthene $C_{15}H_{10}$ must be repre sented by:



As will be seen, this structure was based entirely on degradative oxidation products.

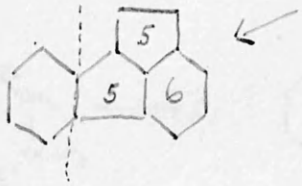
For more than fifty years after this, fluoranthene was forgotten, except for very occasional references, the most important of which was the apparet confirmation of Fittig's formula by the syntheses of isodiphenic acid and fluorenone-1-carboxylic acid by Mayer and Frietag (vii):



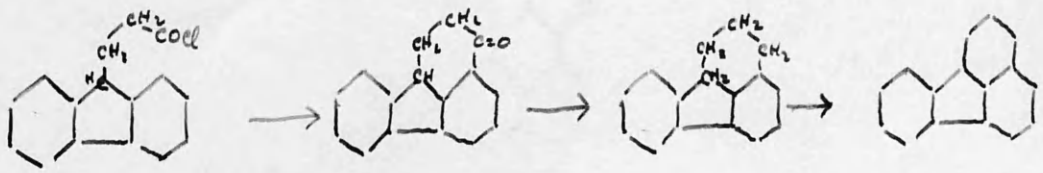
Thus was the structure of fluoranthene apparently determined, and, but for unexpected disagreement with the following theory of multi-planar carbon rings, the hydrocarbon to this day might have been represented by Fittig's formula.

The Sachse-Mohr conception of multi-planar carbon rings, however, permits the following adjacent ring systems to be combined to a benzene nucleus to form a tri-cyclic system: 5 and 6; 6 and 6; 5 and 7; 6 and 7.

Fluoranthene did not agree with this rule as it contained two adjacent five-membered rings attached to the benzene nucleus:



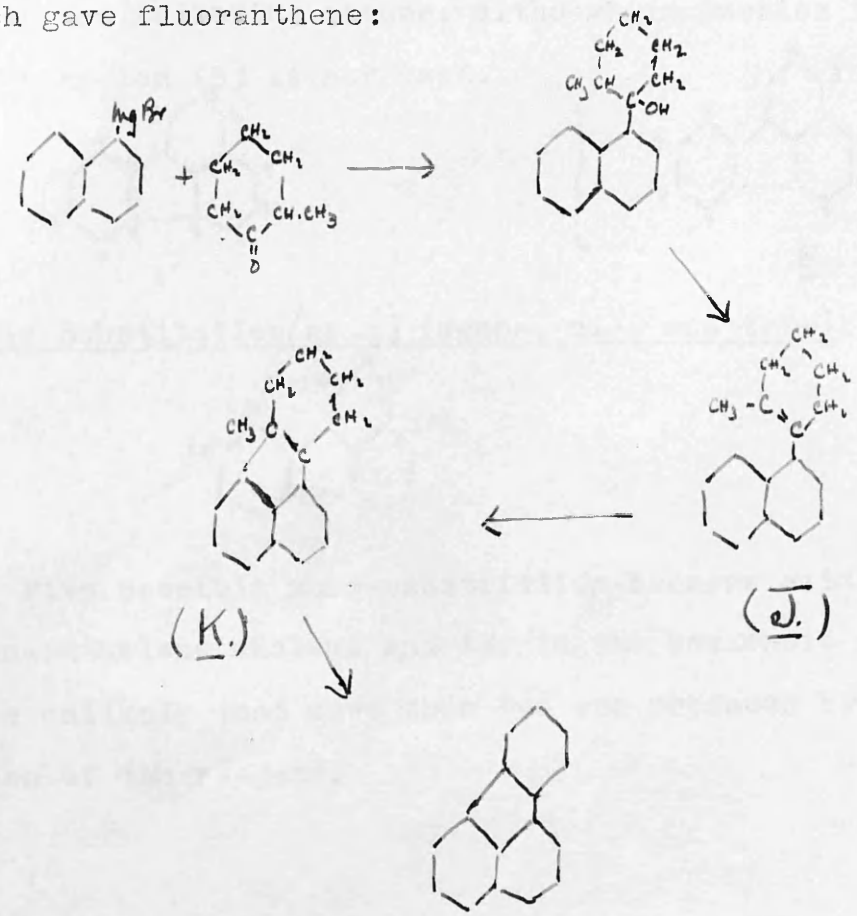
v. Braun and Rath (viii) who had been working on this subject turned their attention to the anomaly, and, assuming fluoranthene to be in reality a naphthalene derivative, (which they calculated would not make much difference in the analytical results), succeeded in synthesising such a substance by the cyclisation of fluorene-9-propionyl chloride (G), reduction of the ketone (H) produced, and finally, dehydrogenation to a hydrocarbon $C_{16}H_{10}$ identical with fluoranthene.



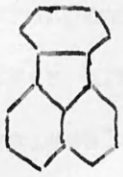
(G.) (H.) Fluoranthene.

Thus was the constitution of fluoranthene proved fully fifty years after its discovery.

A synthesis of fluoranthene which confirms beyond all doubt the existence of a naphthalene nucleus in fluoranthene has been accomplished by Cook and Lawrence (ix), who dehydrated the tertiary alcohol produced by the reaction of α-naphthalene magnesium bromide and 2-methylcyclohexanone, and isomerised the product (J) with aluminium chloride in carbon disulphide to the hydro-fluoranthene (K), dehydrogenation of which gave fluoranthene:

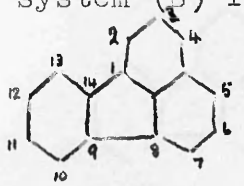


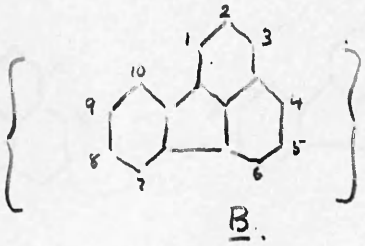
III. THE EFFECT OF THE SYMMETRY OF THE MOLECULE ON THE NUMBER OF SUBSTITUTION ISOMERS; SYSTEMS OF NUMBERING.



The molecule of flouranthene is obviously symmetrical, and therefore the possible number of substitution isomers is greatly lessened.

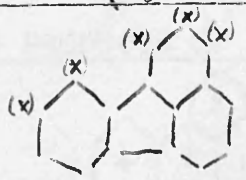
The numbering of such derivatives is generally according to the following scheme, although in America the alternative system (B) is now used.





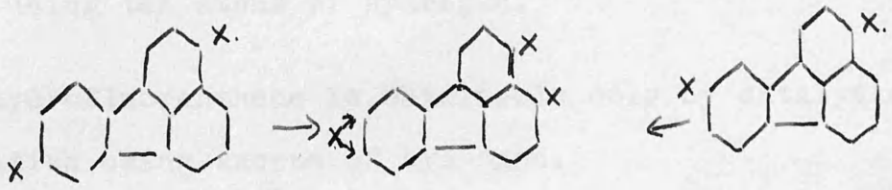
B.

Simple Substitution (by x.) (mono-, di-, and tri-)

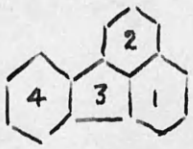


Five possible mono-substitution isomers exist-- three in the naphthalene nucleus and two in the benzenoid system, but it is unlikely that more than two are produced by direct action of the reagent.

There are some twenty-five possible di-substitution isomers of fluoranthene, few of which are likely to be produced directly; a correspondingly larger number of tri-substitution derivatives are possible. The influence of the symmetry of the molecule regarding the number of di-substitution isomers is lost in many cases, yet, as in the last illustration, it is often found that, because of the arrangement of the reactive positions in the fluoranthene nucleus, a third radicle may enter in a position unsubstituted in either di-substituted isomer and yet yield <u>one</u> tri-substituted fluoranthene.



IV. REDUCTION PRODUCTS OF FLUORANTHENE.



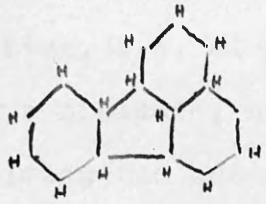
The reduction or hydrogenation (x) of the fluoranthene nucleus, which is easily accomplished, attacks primarily one half of the naphthalene nucleus (ring 1 <u>or</u> 2); further reduction attacks the benzenoid ring (No. 4), and finally the other half of the naphthalene nucleus (ring 2 <u>or</u> 1) to

yield the completely hydrogenated perhydrofluoranthene.

The primary reduction product 1:2:3:4-tetrahydrofluoranthene is best obtained by the action of sodium amalgam at 180°C on the hydrocarbon, but it is apparently also formed by hydriodic acid at 180°C, sodium in moist ether, and catalytic hydrogenation.

1:2:3:4:9:10:11:12:13:14-Decahydrofluoranthene, the second reduction product, is obtained by the reduction of fluoranthene by sodium in alcohol, and by catalytic hydrogenation using ten atoms of hydrogen.

Perhydrofluoranthene is obtainable only by catalytic hydrogenation using excess of hydrogen.

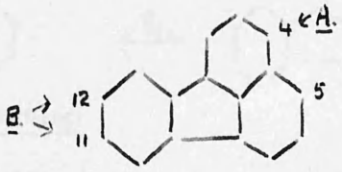


The production of 1:2-dihydrofluoranthene as claimed by Goldschmidt by the restricted action of hydriodic acid and phosphorus on fluoranthene (Cf. p.4.) has not been confirmed.

Fluoranthene. $C_{16}H_{10}$ ⟶ $C_{16}H_{12}$ (?)

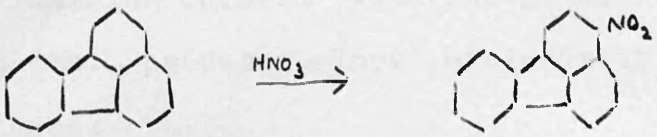
V. THE CHEMISTRY OF FLUORANTHENE.

Positions 4, 11 (or 12), 5, are the most reactive positions in the fluoranthene nucleus: Their degree of reactivity is generally in that order. It will therefore be seen that the same entrant group di-substituting will give the 4:11- and 4:12- isomers, but that further action will give the 4:11:5- tri-substitution derivative only. (Cf. Influence of Symmetry of Molecule.)



Substitution of fluoranthene therefore occurs mostly in the 4- position, i.e. at A; a little of the 11- (or 12-) isomer is always produced, however. But acylation or similar reactions involving the use of anhydrous aluminium chloride, substitute in the 11- (or 12-) position, i.e. at B, preferentially, yielding a little of the 4- isomer as by-product only.

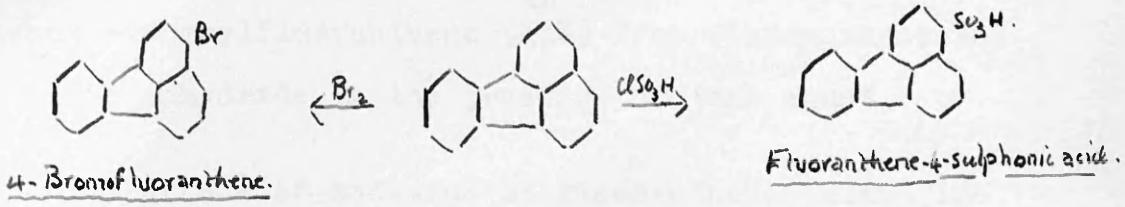
The nitration of fluoranthene (xi) is carried out by the action of fuming nitric acid in glacial acetic acid.



4-Nitrofluoranthene.

4-Nitrofluoranthene is the main product of the reaction, but, is mixed with small quantities of 12-nitrofluoranthene from which it is very difficult to be freed.

Bromination (xi) is best accomplished by direct substitution in ultra-violet light using carbon-disulphide as a solvent and in the presence of traces of phosphorus tribromide. The product is almost exclusively 4-bromofluoranthene.

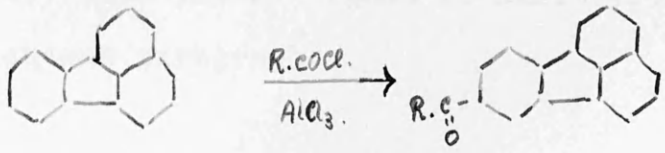


4-Bromofluoranthene. Fluoranthene-4-sulphonic acid.

Fuming sulphuric acid produces from fluoranthene a mixture of fluoranthene-4-sulphonic acid and isomeric disulphonic acids.

v. Braun and Manz (xi), who are the main workers in Fluoranthene Chemistry at present, state that fluoranthene-4-sulphonic acid is best prepared by the action of chlorosulphonic acid in chloroform at -15°C.

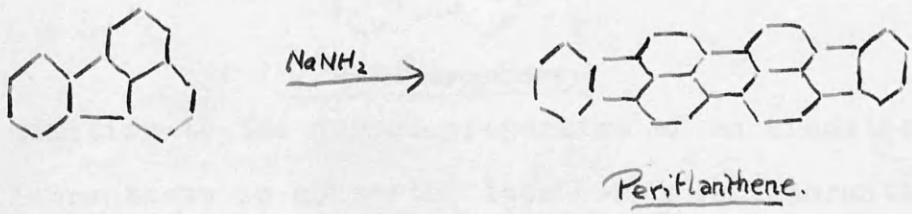
v. Braun, Manz, and Kratz (xii), showed that acylation of fluoranthene, i.e. the reaction in the presence of anhydrous aluminium chloride with phosgene, acetyl- and benzoyl-chlorides etc., produced almost exclusively 11-substituted fluoranthenes:



Where R = Cl, CH_3, Φ etc.

This strange influence of aluminium chloride on the orientation is also exhibited by the production of o'-carboxy-benzoylfluoranthene (xii) from fluoranthene and phthalic anhydride in the presence of that agent.

The effect of sodamide on fluoranthene (xiii) is curious. Instead of the expected 'amination' of the hydrocarbon as occurs with naphthalene (xiv) two molecules of fluoranthene link with the elimination of hydrogen. The name periflanthene has been suggested by v. Braun and Manz for the hydrocarbon produced.



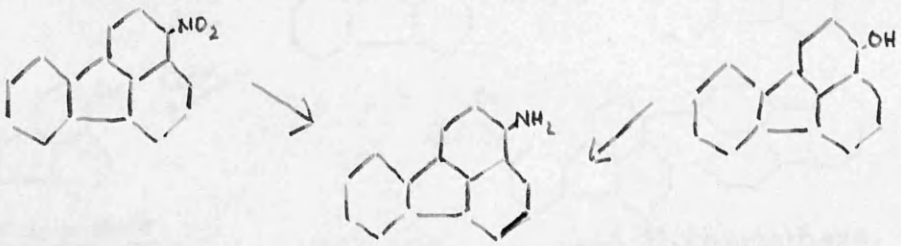
Periflanthene.

Structural proofs (where required) of the orientation in nuclear substitution of fluoranthene are obtained by conversion of the entrant group to a known derivative, or by degradative oxidation by which method characteristic compounds

are formed. This latter method is dealt with exclusively is a subsequent paragraph.

VII. PROPERTIES OF FLUORANTHENE DERIVATIVES.

4-Nitrofluoranthene on reduction yields 4-aminofluoranthen an important amine which is used for identification of position substitution mentioned in the previous paragraph. Because of the difficulty in purifying the 4-nitrofluoranthene, however, the preparation of the amine by this method is wasteful and has been superceded by the preparation from 4-hydroxyfluoranthene by alcoholic ammonia under pressure.

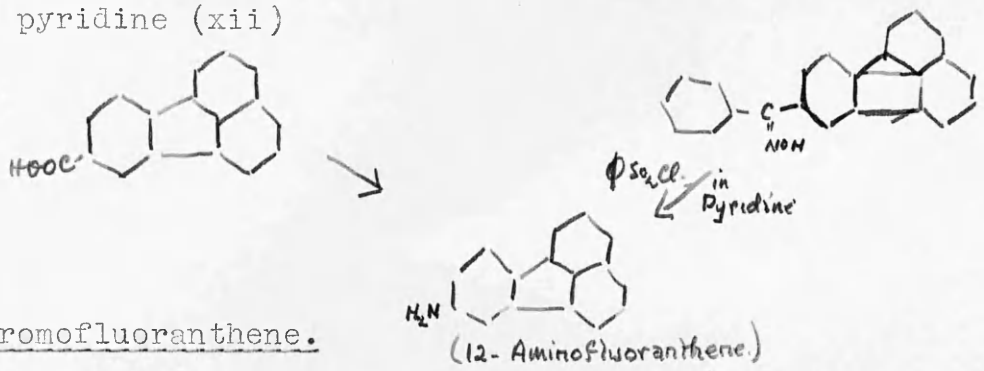


4-Aminofluoranthene.

In addition to the normal properties of an aromatic amine, 4-aminofluoranthene is converted into 4-hydroxyfluoranthene by dilute hydrochloric acid under pressure. Reduction with sodium amalgam gives an ar-aminotetrahydrofluoranthene.

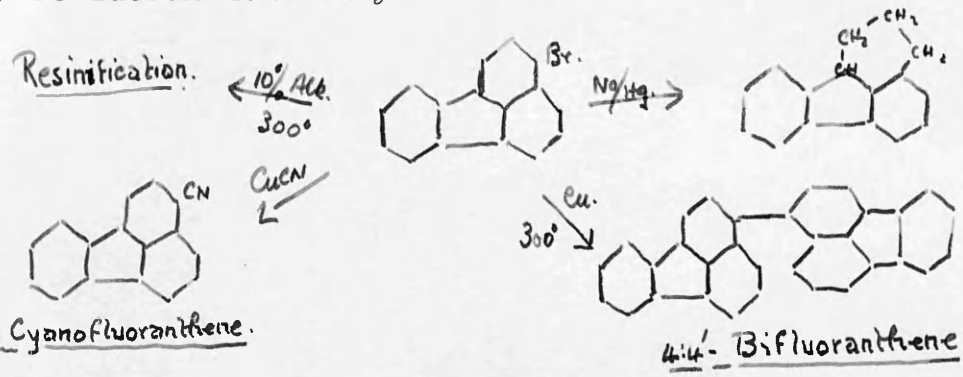
The isomeric 12-aminofluoranthene is either prepared from the 12-carboxylic acid through the intermediate, hydrazide, azide, urethane, etc., or by the rearrangement of the

oxime of 12-benzoylfluoranthene by benzene sulphonyl chloride and pyridine (xii)



4-Bromofluoranthene.

Although 4-bromofluoranthene is unable to form a Grignard reagent, the bromine atom appears to be somewhat loosely combined and easily eliminated by reducing agents, e.g. sodium amalgam at room temperature yields 1:2:3:4-tetrahydrofluoranthene only.



Yet the bromine atom is unaffected by 5%-10% alkali at 200°C and the compound resinifies with the same reagent at 300°C. As expected, cuprous cyanide yields 4-cyanofluoranthene and copper bronze at 300°C 4:4'-bifluoranthyl.

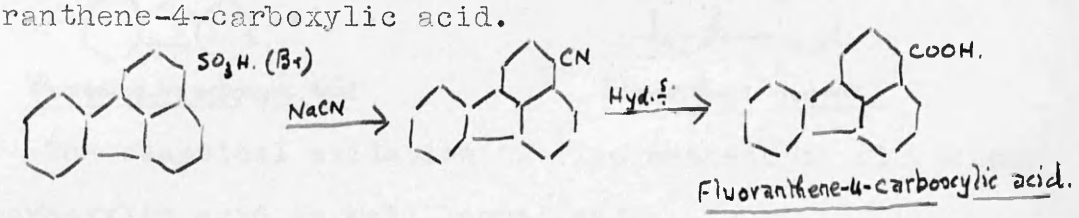
4-Hydroxyfluoranthene. (xi)

A may be prepared from either the 4-amino- (as stated) or

by the fusion of the 4-sulphonic acid by caustic potash in the normal manner.

4-Cyanofluoranthene. (xi).

Prepared as described from the 4-bromofluoranthene, or from the 4-sulphonic acid by fusion with sodium or potassium cyanide, is hydrolised by dilute hydrochloric acid to fluoranthene-4-carboxylic acid.

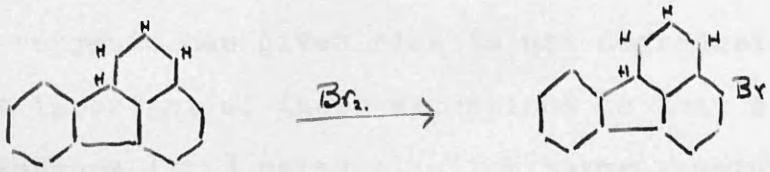


Fluoranthene-4-carboxylic acid.

This is the only satisfactory method of preparation of the acid, as, although it is produced to some extent in the preparation of the 12-carboxylic acid, it cannot be prepared from it satisfactorily.

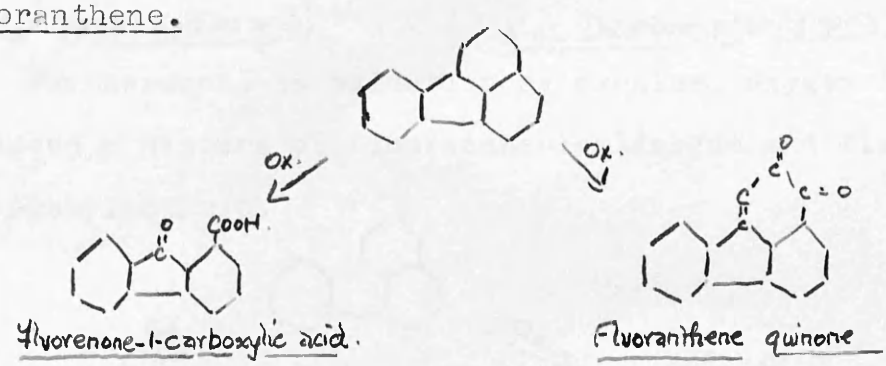
1:2:3:4-Tetrahydrofluoranthene.

Substitutes in normal reactions as does fluoranthene, e.g. bromination yields 5-bromo-1:2:3:4-tetrahydrofluoranthene



VII. DEGRADATION OF FLUORANTHENE AND DERIVATIVES BY OXIDATION.

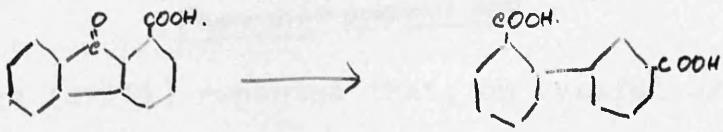
Fluoranthene.



Fluorenone-1-carboxylic acid. Fluoranthene quinone

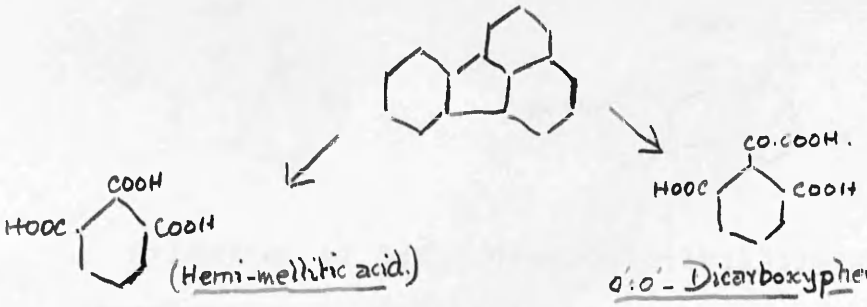
The classical oxidation of fluoranthene to fluorenone-1-carboxylic acid is well known (xv).

The constitution of the ketonic acid has been proved by synthesis, and the illustrated formula allocated to the quinine. Fittig and Gebhard (v), had further degraded this keto-acid to isodiphenic acid (or 2:3'-diphenic acid).

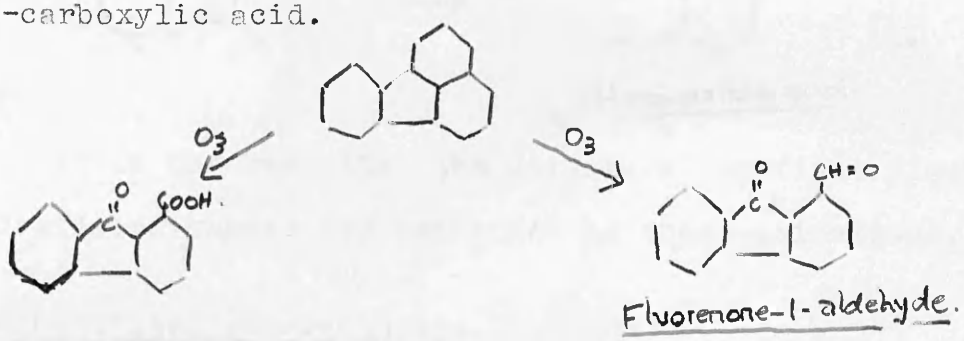


2:3'-Diphenic acid.

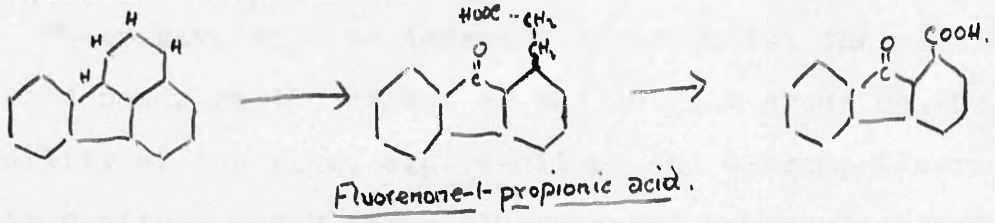
In recent times the oxidation of the hydrocarbon by various reagents has given rise to new degradation products. The most important of these oxidations is that of Randall and co-workers (xvi) using alkaline permanganate of potash by which reagent they obtained the final degradation product, hemimellitic acid, and also o'-6'-dicarboxyphenyl-glyoxylic acid:



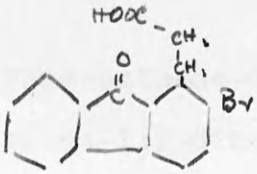
Furthermore, an oxidation by ozonised oxygen (xvii) produced a mixture of fluorenone-1-aldehyde and fluorenone-1-carboxylic acid.

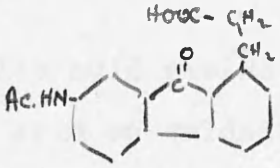


The Hydrofluoranthenes.

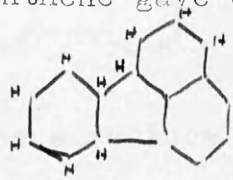


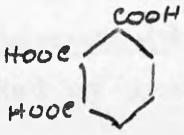
Krüber (xviii) reported that, on careful oxidation, 1:2:3:4-tetrahydrofluoranthene yielded fluorenone-1-propionic acid as the first product of oxidation. Fluorenone-1-carboxylic acid was subsequently obtained if the reaction was carried further. v. Braun, Manz and Kratz (xii) extended this oxidation to cover the derivatives of 1:2:3:4-tetrahydrofluoranthene, e.g. 5-bromofluorenone-1-propionic acid and 7-acetylaminofluorenone-1-propionic acid were obtained from their respective hydrofluoranthenes.





Oxidation of 1:2:3:4:9:10:11:12:13:14:decahydro-fluoranthene gave only hemimellitic acid. (xii).



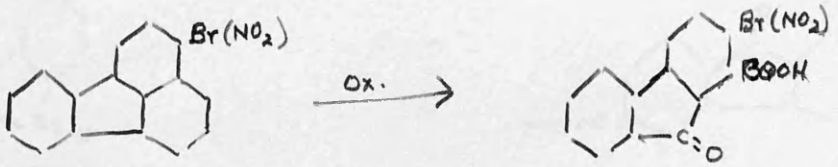


Hemi-mellitic acid.

It is observed that the structural configurations of the hydrofluoranthenes are confirmed by these oxidations.

4-Substituted Fluoranthenes.

These give rise to degradative products, the nature of which depends on the effect of the entrant group on the stability of the ring, e,g. 4-nitro- and 4-bromo-fluoranthenes yield 2-nitro- and 2-bromo-fluorenone-1-carboxylic acids:

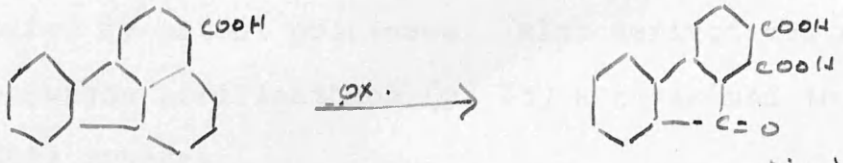


While those groups which render the ring more sensitive to oxidation, naturally yield fluorenone-1-carboxylic acid alone.

The Fluoranthene Carboxylic Acids.

These yield fluorenone dicarboxylic acids on oxidation. (xii

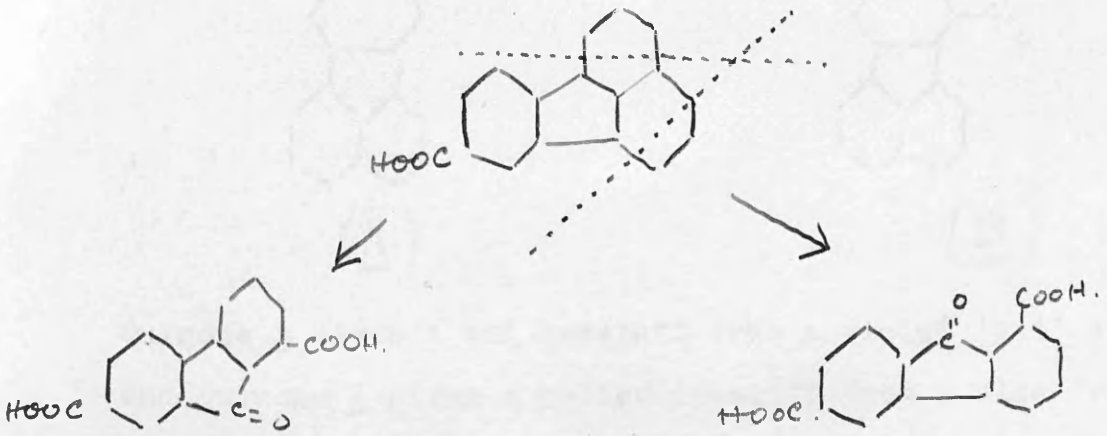
Fluoranthene-4-carboxylic acid yields exclusively fluorenone-1:2-dicarboxylic acid on oxidation, because of the stabilising effect mentioned previously.



Fluorenone-1:2-dicarboxylic acid.

The structure has been confirmed by synthesis. (xii).

Fluoranthene-12-carboxylic acid presents a different problem: Either part of the naphthalene nucleus in fluoranthene may oxidise, and therefore two isomeric fluorenone-dicarboxylic acids are obtained:



Fluorenone-1:7-dicarboxylic acid.

Fluorenone-1:6-dicarboxylic acid.

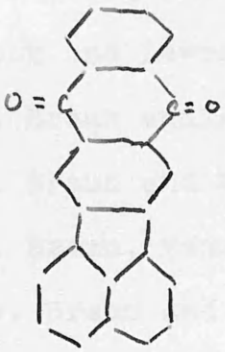
VIII. FLUORANTHENE DERIVATIVES IN DYE CHEMISTRY.

Within recent years several Patents have been taken out covering certain fluoranthene derivatives as Dyestuff Intermediates. It is unlikely that fluoranthene derivatives have

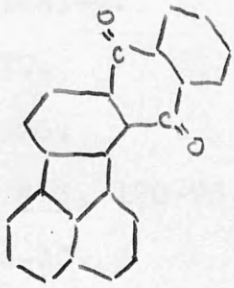
yet been used in that industry.

These derivatives are mainly the hydroxysulphonic acids, hydroxycarboxylic acids, amines, etc. which are mostly all prepared by patent processes. Also derivatives of the hydrocarbon periflanthene (p. 13) are claimed to be of use in this sphere.

The complex quinones obtained from 12-o-carboxybenzoyl-fluoranthene (p.13) by ring closure have been shown to possess vat-dying properties:



(A.)



(B.)

Quinone A gives a red dyestuff from a violet 'vat' solution, and quinone B gives a yellow dyestuff from a blue 'vat'.

Similar reactions on the condensation product of periflanthene and phthalic anhydride yields similar complex quinones.

I N D E X .

(i) Goldschmidt: Ber. 10, 2022-30.

(ii) Fittig and Gebhard: Ber. 10, 2141.

(iii)Atterberg: Ber. 11, 1224.

(iv) Goldschmidt: Wien. Akad. Ber. 81, 415-29.

(v) Fittig and Gebhard: Lieb. Ann. 193, 142-60.

(vi) Fittig and Lippmann: Ber. 12, 163-5.

(vii)Mayer and Frietag: Ber. 54B 347-57.

(viii)v. Braun and Anton: Ber. 62B 145-51.

(ix) Cook and Lawrence: J.C.S. 1936, 1431-4.

(x) v. Braun andManz: Ber. 63B 2608-12.

(xi) v. Braun and Manz: Ann. 488, 111-26.

(xii)v. Braun, Manz, and Kratz: Ann. 496, 170-96.

(xiii)v. Braun and Manz: Ber. 70B 1603-10.

(xiv)Sachs: Ber. 39, 3023.

(xv) Fieser and Seligman: J.A.C.S. 57 (2), 2174.

(xvi)Randall & Coworkers: Proc.Roy.Soc. A, 165, 432-52.

(xvii)A.G.Farb. (Patent) 817, 584, Sept. 6, 1937.

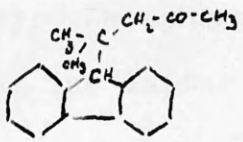
(xviii)Krüber: Ber. 64B 84-5.

PART II.

I N T R O D U C T I O N .

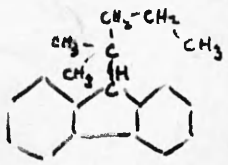
I N T R O D U C T I O N .

Fluorene had been condensed with acetone in the presence of anhydrous potassium hydroxide to yield β-β-β-9-fluorenyldimethyl-methyl-ethyl ketone:



(Maitland and Tucker, J.C.S. 1929, 2559; France, Maitland and Tucker, J.C.S. 1937, 1739.)
The structure of this substance had been proved by synthesis.

The ketone underwent some curious reactions: Reduction by hydriodic acid in acetic acid gave, instead of the expected 9-fluorenyl-methyl-pentane,
a white hydrocarbon $C_{19}H_{20}$, m.p.103°C;

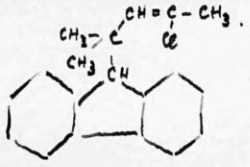


also dry hydrobromic acid in acetic acid produced a substance which decomposed with evolution of hydrobromic acid to yield another white hydrocarbon $C_{19}H_{18}$, m.p. 77°C., which could be reduced to the $C_{19}H_{20}$, m.p. 103°C., mentioned before by hydriodic acid in acetic acid.

Oxidation of the hydrocarbon $C_{19}H_{18}$ gave a ketonic acid of the empirical formula $C_{19}H_{18}O_3$, which contained an acetyl group (-CO.CH_3), while $C_{19}H_{20}$, on oxidation with sodium dichromate in dilute sulphuric acid had yielded traces of fluorenone-1-carboxylic acid.

The reactions of zinc chloride and phosphorus pentoxide on the ketone had also produced curious results: With zinc chloride at 250°C. two products were formed-- the white hydrocarbon $C_{19}H_{20}$, m.p. 103°C., previously described, and a yellow hydrocarbon, m.p. 131°C., of alleged empirical formula $C_{16}H_{14}$ (?). Phosphorus pentoxide under the same conditions yielded the latter substance, m.p. 131°C. alone.

Nitration of the ketone yielded a mono-nitrated derivative m.p. 112°C., of unknown structure, while phosphorus pentachloride produced a chlorohydrocarbon $C_{19}H_{19}Cl$, m.p. 80°C., from the ketone. This latter compound was oxidisable to fluorenone, and has probably the illustrated structure:



PART III.

GENERAL EXPERIMENTS ON THE PRODUCTS DERIVED FROM

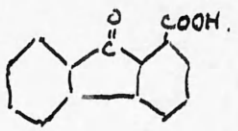
β-β-β-9-FLUORENYLDIMETHYL-METHYL-ETHYL KETONE.

GENERAL EXPERIMENTS ON THE PRODUCTS DERIVED FROM β-β-β-9-FLUORENYLDIMETHYLMETHYLETHYL KETONE.

With the object of determining the structures of the hydrocarbons $C_{19}H_{18}$, $C_{19}H_{20}$, and $C_{16}H_{14}$ (?), referred to before, the problem of their degradation by oxidation was studied.

While working with the ketonic acid $C_{19}H_{18}O_3$ (Cf. Part II) obtained from $C_{19}H_{18}$, a successful oxidation to fluorenone-1-carboxylic acid was accomplished by using sodium dichromate in acetic acid; this led to similar oxidations being attempted on the hydrocarbons.

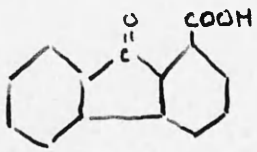
KETO-ACID. $C_{19}H_{18}O_3$ —OXID.^{n} $Na_2Cr_2O_7$→



Fluorenone-1-carboxylic acid.

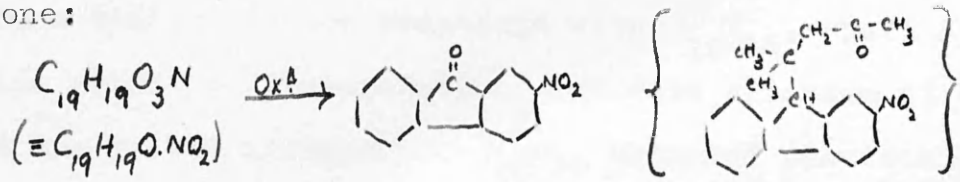
All three hydrocarbons were found to yield the same product, fluorenone-1-carboxylic acid, $C_{19}H_{18}$ in 65% of theory, and the others in smaller quantities.

$C_{19}H_{18}$
$C_{19}H_{20}$
$C_{16}H_{14}$?
} —$Na_2Cr_2O_7$→



Fluorenone-1-carboxylic acid.

Oxidation of the nitro-derivative of β-β-β-9-fluorenyldimethylmethylethyl ketone (Cf. Part II) yielded 2-nitrofluorenone:

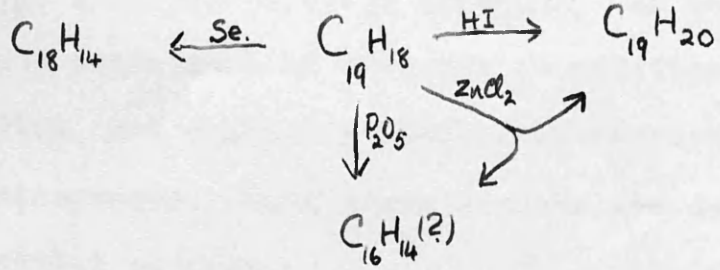


The compound must therefore have the structure β-β-β-9-(2-nitro-)fluorenyldimethylmethylethyl ketone.

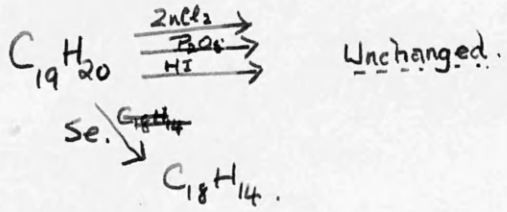
The chemical changes of these hydrocarbons under the influence of certain reagents were made the subject of considerable investigation.

It was found that $C_{19}H_{18}$ gave, as did the original ketone (Cf. Part II), $C_{19}H_{20}$ on reduction with hydriodic acid in acetic acid; $C_{16}H_{14}$ (?) and $C_{19}H_{20}$ on heating with zinc chloride at 250°C., and $C_{16}H_{14}$ (?) alone on heating at the same temperature with phosphorus pentoxide.

Furthermore, $C_{19}H_{18}$ yielded a yellow hydrocarbon $C_{18}H_{14}$, m.p. 113°-115°C., similar in appearance to $C_{16}H_{14}$ (?), on dehydrogenation with selenium at 320°C.

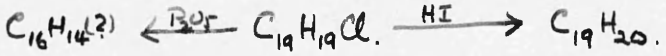


The hydrocarbon $C_{19}H_{20}$ proved to be unaffected by hydriodic acid, zinc chloride, or phosphorus pentoxide, under conditions similar to the reactions with $C_{19}H_{18}$, apart from a certain amount of decomposition, but with selenium at 320°C. yielded the yellow hydrocarbon $C_{18}H_{14}$ obtained previously from $C_{19}H_{18}$.



$C_{16}H_{14}$ (?) was unaffected by any of these reagents.

It was also observed that the chlorohydrocarbon $C_{19}H_{19}Cl$ obtained by the action of PCl_5 on the original ketone (Cf. Part II) gave, as the ketone, $C_{19}H_{20}$ with hydriodic acid in acetic acid, and $C_{16}H_{14}$ (?) with phosphorus pentoxide at 250°C



N.B. As these experiments required considerable quantities of $C_{19}H_{18}$, $C_{19}H_{20}$, and $C_{16}H_{14}$ (?), improvements on the original preparations were sought, both in yields and in extraction from the crude reaction medium.

While no improvement was effected in the production of $C_{19}H_{18}$, an improved yield of $C_{19}H_{20}$ was obtained by altering the concentrations of reagents in solution during the preparation, and a greatly simplified extraction of $C_{16}H_{14}$ (?) was discovered. Both these methods are described in the experimental section.

PART IV.

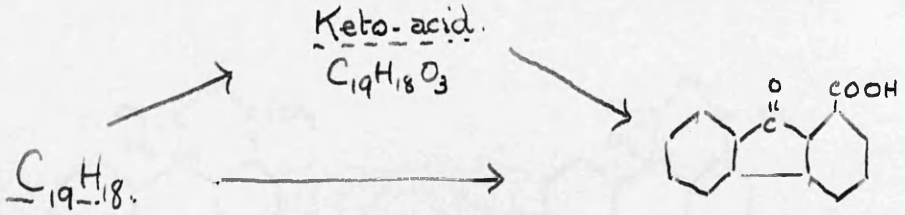
ELUCIDATION OF THE STRUCTURES OF THESE COMPOUNDS.

ELUCIDATION OF THE STRUCTURES OF $C_{19}H_{18}$, $C_{19}H_{20}$, $C_{16}H_{14}$(?), AND $C_{18}H_{14}$.

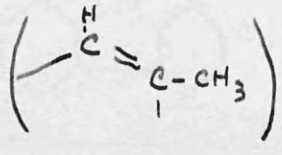
(i) $C_{19}H_{18}$ And $C_{19}H_{20}$.

Since a close relationship exists between the two hydrocarbons $C_{19}H_{18}$ and $C_{19}H_{20}$ shown by the reduction of the former to the latter, it is only necessary to determine the structure of $C_{19}H_{18}$, as $C_{19}H_{20}$ is obviously the completely saturated (in an 'ethylenic' sense) 'dihydro'-$C_{19}H_{18}$.

From Parts II and III it is observed that $C_{19}H_{18}$ can either be oxidised to a ketonic acid $C_{19}H_{18}O_3$, which in turn is oxidisable to fluorenone-1-carboxylic acid or may be directly oxidised to that substance.



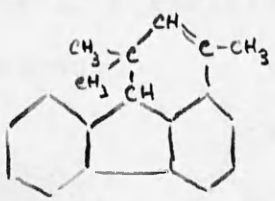
This keto-acid $C_{19}H_{18}O_3$ has lost no carbon atoms in the preparation from $C_{19}H_{18}$ and contains an 'methyl ketone' group. Therefore it must have been produced by the oxidation of a tri-substituted ethylenic link of the following nature:

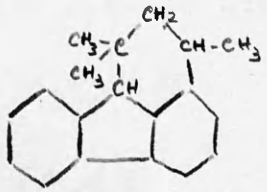


The oxidation of this acid and the hydrocarbon $C_{19}H_{18}$ to fluorenone-1-carboxylic acid proves that ring closure of the ketone β-β-β-9-fluorenyldimethylmethylethyl ketone must have taken place during the formation of $C_{19}H_{18}$.

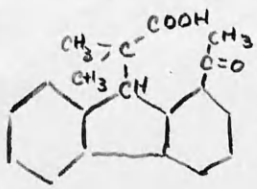
As will be seen from the formula for the ketone ($C_{19}H_{20}O$), it is impossible for ring closure to occur and yet leave the above ethylenic linkage outwith the ring.

Therefore, the only feasible structure for $C_{19}H_{18}$ is 2:2:4-trimethyl-1:2-dihydrofluoranthene; $C_{19}H_{20}$ must be 2;2:4-trimethyl-1:2:3:4-tetrahydrofluoranthene,


($C_{19}H_{18}$)

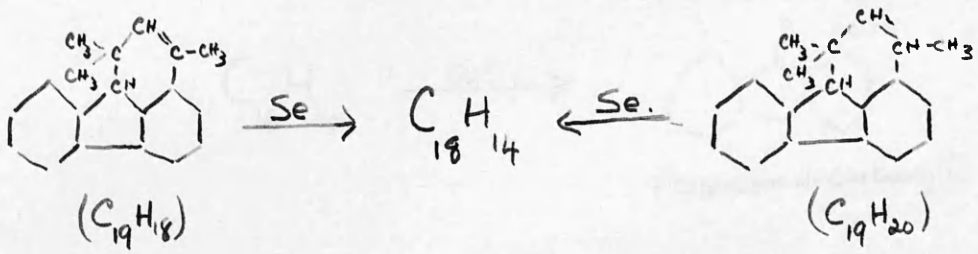

($C_{19}H_{20}$)

and the ketonic acid $C_{19}H_{18}O_3$,



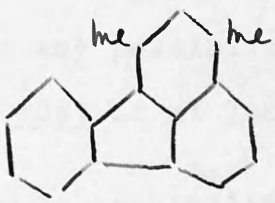
(ii) $C_{18}H_{14}$.

As the structures 2:2:4-trimethyl-1:2-dihydro- and 2:2:4-trimethyl-1:2:3:4-tetrahydro- fluoranthene have been allocated to $C_{19}H_{18}$ and $C_{19}H_{20}$ respectively, the constitution of the compound derived from both by the dehydrogenating action of selenium can be easily determined:



$(C_{19}H_{18})$ $(C_{19}H_{20})$

As one carbon atom is lost during the reaction, it is apparent that with $C_{19}H_{18}$ methane, and with $C_{19}H_{20}$ methane and hydrogen have been lost. Therefore, the only possible structure for $C_{18}H_{14}$ must be 2:4-dimethyl-fluoranthene:



$(C_{18}H_{14})$

2:4-Dimethylfluoranthene.

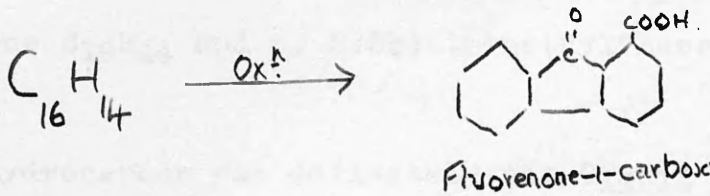
(iii) $C_{16}H_{14}$ (?).

The hydrocarbon $C_{16}H_{14}$ (?) was not unsaturated in an

aliphatic sense, nor could it be dehydrogenated by any of the reagents tried.

These facts, together with its extreme stability with regard to distillation etc., gave definite evidence that the structure was purely 'aromatic' in character.

Oxidation of the hydrocarbon yielded fluorenone-1-carboxylic acid ($C_{14}H_8O_3$)



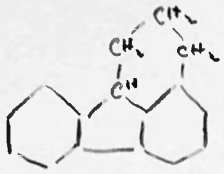
Fluorenone-1-carboxylic acid.

Therefore, 14 carbon atoms of the 16 required by the alleged $C_{16}H_{14}$ (?) are placed; also 7 of the hydrogen atoms are placed.

The remaining two carbon atoms must form a ring between the 9- and 1- positions indicated by the keto- and carboxylic acid- groups. (The number of hydrogen atoms precludes any possibility of open chain structure).

This ring must be at least six membered. (Cf. Part I p.6)

Thus the only possibility for $C_{16}H_{14}$ is tetrahydrofluoranthene, which is obviously impossible as the alleged $C_{16}H_{14}$ cannot be dehydrogenated, therefore the empirical formula $C_{16}H_{14}$ must be erroneous.

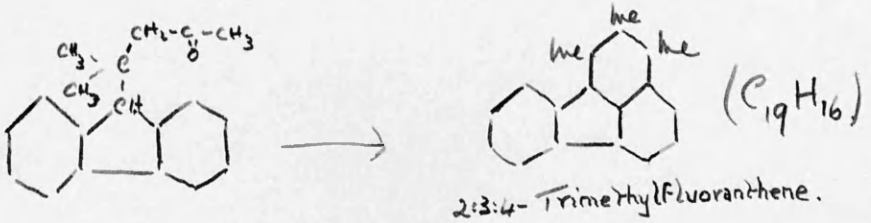


(Tetrahydrofluoranthene)

As the hydrocarbon must have a six-membered ring in the positions indicated, it must be a derivative of fluoranthene.

From the analytical results and structure of the ketone, two fluoranthenes are possible: 1. 2:4-dimethyl fluoranthene $C_{18}H_{14}$ and 2. 2:3:4-trimethylfluoranthene $C_{19}H_{16}$.

The hydrocarbon was definitely not $C_{18}H_{14}$ which had been prepared by other means (Cf. previous pages) and therefore it must be $C_{19}H_{16}$ i.e. 2:3:4-trimethyl-fluoranthene, and must have been produced from the original ketone by migration of a methyl group (instead of elimination) during the course of the reaction.



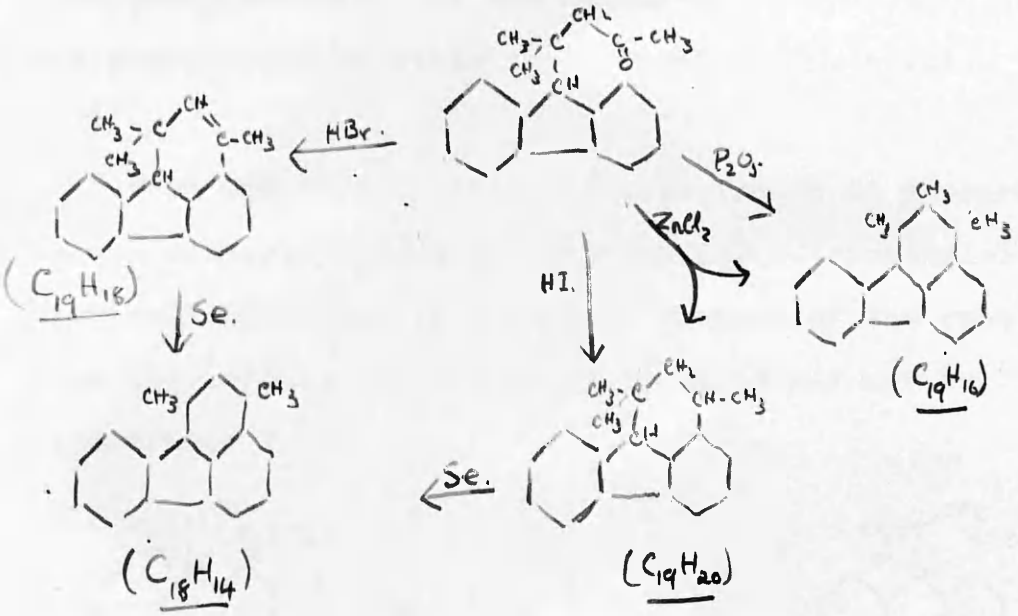
$(C_{19}H_{16})$

2:3:4- Trimethylfluoranthene.

PART V.

MECHANISM OF THE REACTIONS PRODUCING THESE SUBSTANCES.

THE MECHANISM OF THE REACTIONS PRODUCING THESE FLUORANTHENE DERIVATIVES FROM β-β-β-9-FLUORENYLDIMETHYLMETHYLETHYL KETONE.

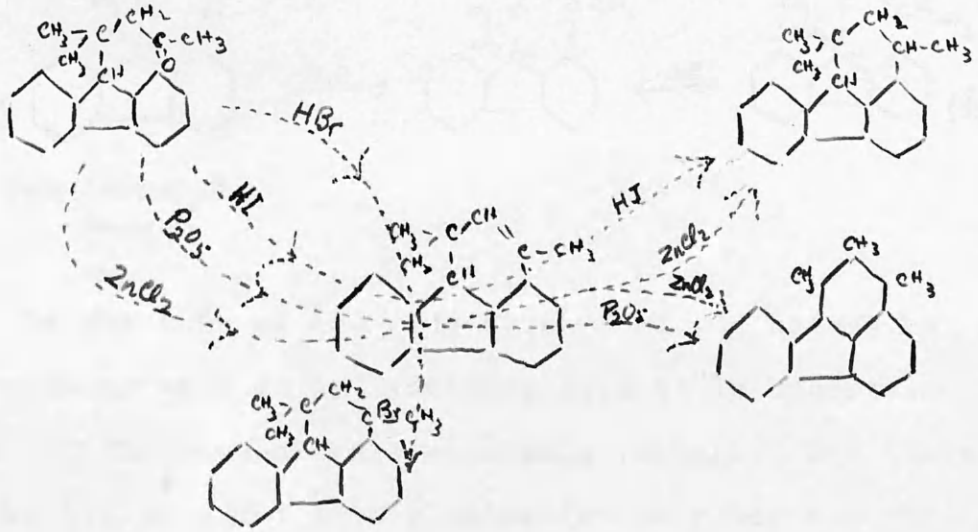


Evidence with regard to the mechanism of the reactions illustrated above can be deduced from the results described in Part III.

Firstly, it had been found that 2:2:4-trimethyl-1:2-dihydrofluoranthene ($C_{19}H_{18}$) yielded the same products of reaction from the same reagents under conditions identical with those under which these products were derived from the original ketone (Cf. pp.26.); and secondly, that, also

similarly to the ketone, 2:2:4-trimethyl-1:2:3:4-tetrahydrofluoranthene ($C_{19}H_{20}$), and 2:3:4-trimethylfluoranthene ($C_{19}H_{16}$) were produced from 1:1:1-(9)-fluorenyldimethyl-3-chloro-$\Delta^{2,3}$-n-butene by the reactions of hydriodic acid and phosphorus pentoxide respectively. (Cf. pp.27.).

From the former series of experiments it appears to be a reasonable deduction that the 2:2:4-trimethyl-1:2-dihydrofluoranthene is the first product of the reactions from the ketone, the mechanism of which may now be illustrated thus:

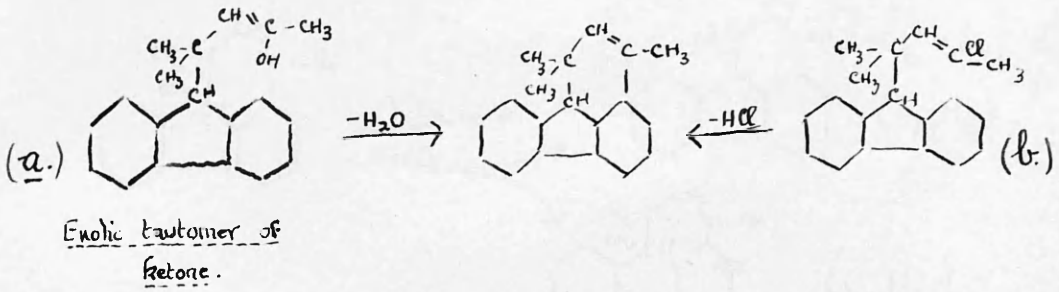


(The dotted line may be taken as indicating the course of the reaction.)

The ring-closure of the ketone to this 'intermediate' may occur in either of two ways:

(a) By the elimination of water between the 'enolic' tautomer of the ketone and the 1- position of the fluorene nucleus, or

(b) by the elimination of a halogen acid from similar positions. (Cf. pp. 27).

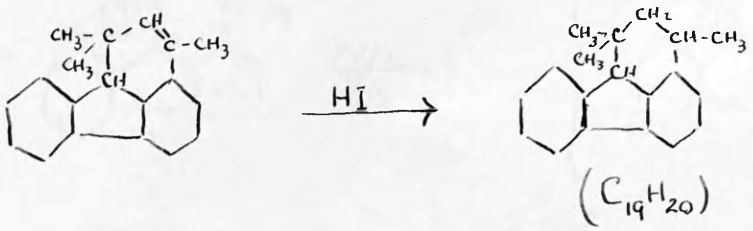


Enolic tautomer of ketone.

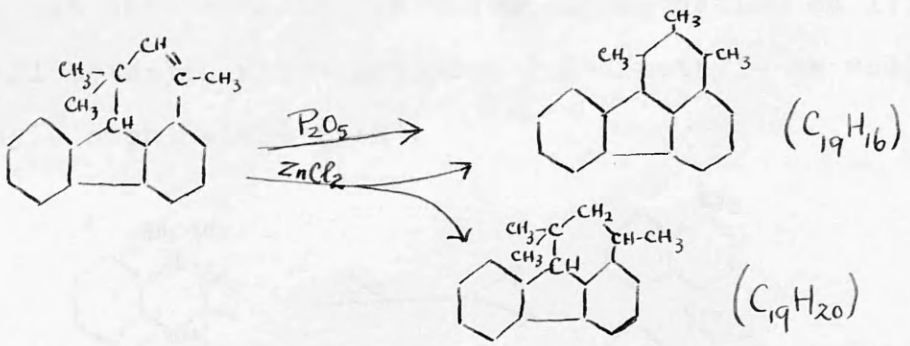
In the case of the ring-closure of the ketone by hydrobromic acid or by hydriodic acid it is uncertain which of those means were employed, (a) or (b), but there can be little doubt that elimination of water occurred in the reaction with zinc chloride or phosphorus pentoxide.

Subsequent formation of the various fluoranthene derivatives from the intermediate 2:2:4-trimethyl-1:2:3:4-dihydrofluoranthene is more complicated, with the exception

of the production of 2:2:4-trimethyl-1:2:3:4-tetrahydrofluoranthene ($C_{19}H_{20}$) by simple reduction of the double bond by the hydriodic acid:



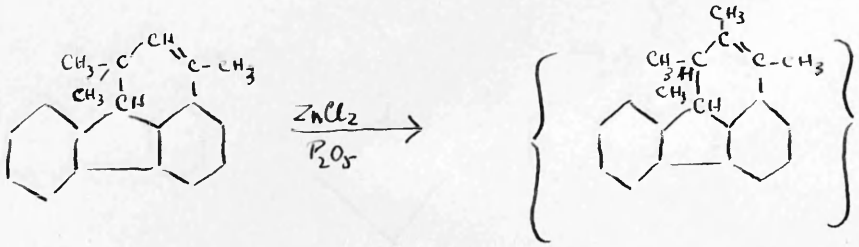
The reactions with zinc chloride and phosphorus pentoxide cannot be explained so simply:



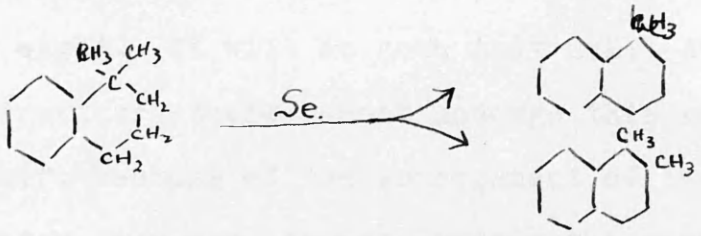
(It was proved that the 'tetrahydrofluoranthene' was not an 'intermediate' but an 'end-product' of the reaction, by the observation that it was almost unaffected by the reagents under the conditions of the reaction.)

The first effect of both the zinc chloride and the phosphorus pentoxide appears to be the causing of migration

of one of the methyl groups of the 'gem'-dimethyl grouping:



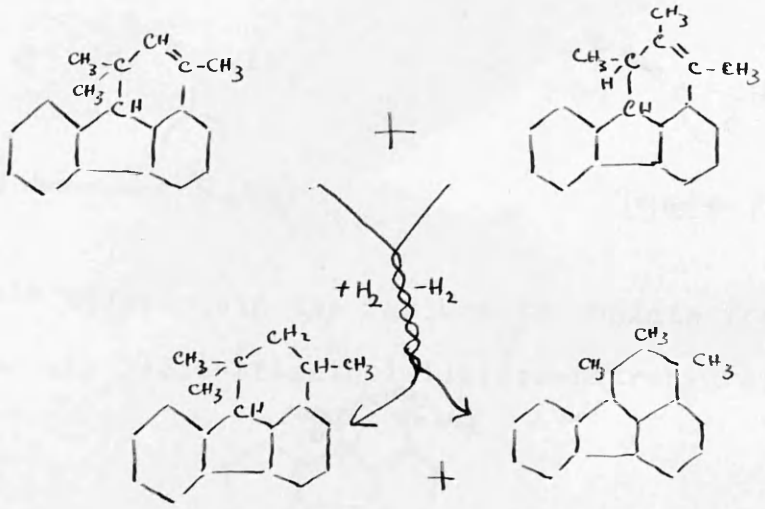
The migration of 'gem'-dimethyl groups is well - known in the terpene compounds. Lately, a similar migration has been reported in the dehydrogenation of 1:1-dimethyl tetralin which produces 1:2-dimethyl- as well as 1-methyl- naphthalene (xix).

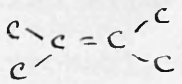


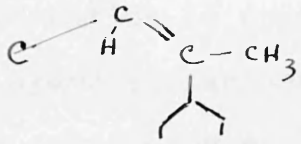
Previous references to similar migrations have been observed. (xx, & xxi).

After migration has taken place the effects of the zinc chloride and phosphorus pentoxide do not follow the same course: With zinc chloride, the migrated product apparently undergoes an auto-oxidation-reduction with the

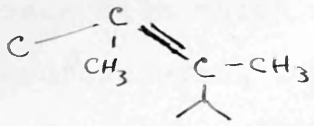
unmigrated 'intermediate' 2:2:4-trimethyl-1:2-dihydro-fluoranthene:-



This hypothesis is not so improbable as it may appear at first sight. It will be seen that 2:2:4-trimethyl-1:2-dihydrofluoranthene cannot undergo this reaction with itself, because of the arrangement of the methyl groups which, however, do not prevent the rimg from being reduced to the 'tetrahydrofluoranthene'. It is also quite possible that this substance might be reduced more easily than the migration product since the former has a hydrogen atom of the ethylenic system unsubstituted, whilst the latter, with the grouping of the type  , which is known to be resistant to reduction. (xxii).

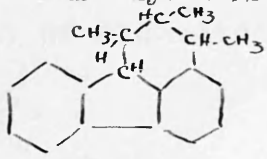


'Intermediate' ($C_{19}H_{18}$)

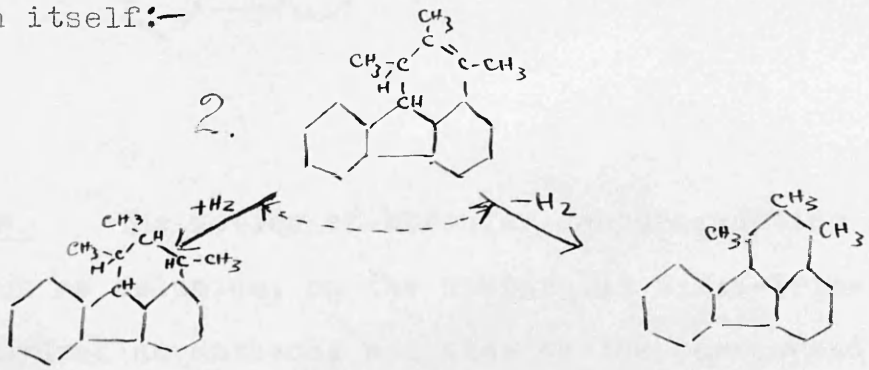


'Migration product'.

This may explain the failure to isolate from the reaction any 2:3:4-trimethyl-1:2:3:4-tetrahydrofluoranthene.



which would be produced by the migration product reacting with itself:—

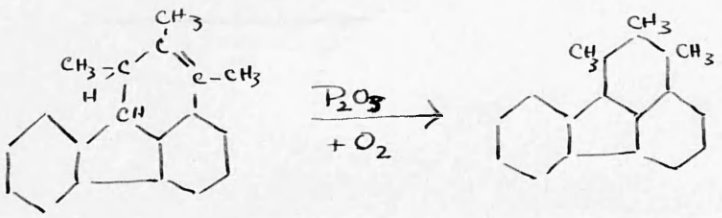


Although the product of reaction with phosphorus pentoxide is identical with one of the products of reaction with zinc chloride, the mechanism of its production is probably not similar. It is considered that in this

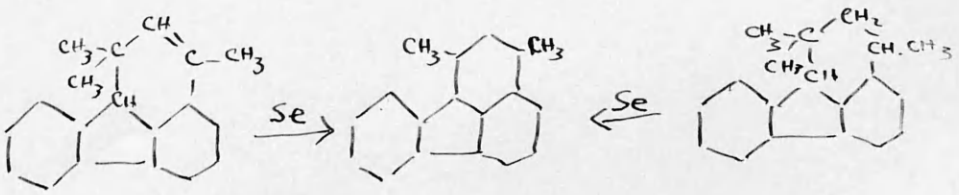
case, the phosphorus pentoxide acts as a weak dehydrogenating agent.

Attention is drawn to the ease with which all known hydrofluoranthenes are dehydrogenated, even with a mild agent such as lead oxide. (xxiii).

The phosphorus pentoxide which may act as $P_2O_3 + O_2$ is much too weak to remove metane from the unmigrated hydrocarbon, but acts on the much more easily oxidisable product of migration:-



N.B. The action of stronger dehydrogenating agents, such as selenium, on the unmigrated 2:2:4-trimethyl-1:2-dihydrofluoranthene, and also on the corresponding 'tetrahydro' derivative, results in the removal of methane and the production of 2:4-dimethylfluoranthene. (xxiv).



Thus, the 'dehydration' of the original ketone with zinc chloride and phosphorus pentoxide must embody three separate reactions:

(1) Ring-closure (dehydration),

(2) rearrangement,

(3a) auto-oxidation-reduction (with $ZnCl_2$),

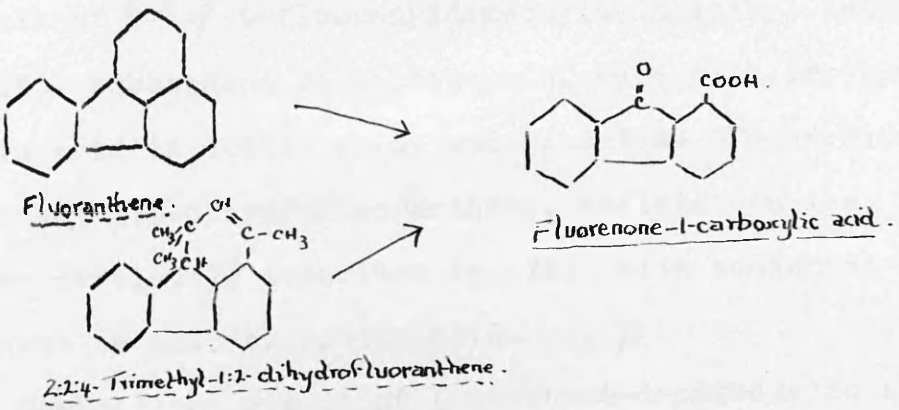
and (3b) dehydrogenation (with P_2O_5).

PART VI.

A NEW METHOD FOR THE PREPARATION OF FLUORENONE-1-CARBOXYLIC ACID (AND SUBSEQUENT 1-SUBSTITUTED FLUORENES) FROM FLUORENE.

A NEW METHOD OF PREPARATION OF FLUORENONE-1-CARBOXYLIC ACID (AND SUBSEQUENT 1-SUBSTITUTED FLUORENES) FROM FLUORENES.

The general excellence of the yields of fluorenone-1-carboxylic acid obtained by the degradative oxidations of the hydrofluoranthenes previously mentioned, especially the oxidation of 2:2:4-trimethyl-1:2-dihydrofluoranthene, led to the investigation into the practicability of such an oxidation on a larger scale as a new method of preparation of the above acid.



The uses of the acid may be briefly mentioned. It is the only practicable source of 1-substituted fluorenes, and has up till now been obtained solely by the oxidation of the comparatively inaccessible hydrocarbon fluoranthene (xxv), apart from synthetic methods

unsuitable for preparative purposes.

Recently a synthesis of a polycyclic hydrocarbon was carried out using fluorenone-1-carboxylic acid as a starting material. (xxv).

This new preparation of fluorenone-1-carboxylic acid, although it involved the oxidation of a hydrofluoranthene, had for its starting material the parent hydrocarbon fluorene, and therefore is the first preparation of the acid from fluorene itself.

Briefly, the method consisted of the preparation in bulk of β-β-β-9-fluorenyldimethylmethylethyl ketone (pp.23), subsequent ring-closure of same with dry hydrobromic acid in acetic acid, and oxidation of the 2:2:4-trimethyl-1:2-dihydrofluoranthene, isolated in the manner previously described (pp.23), with sodium dichromate in glacial acetic acid.

The optimum yields of fluorenone-1-carboxylic acid never exceeded 25-30 g. from 100 g. of fluorene originally used.

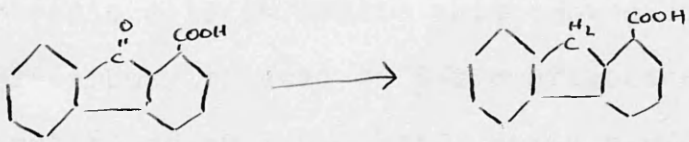
The preparation had both advantages and drawbacks when compared with the existing method. Its advantage lay in the fact that the starting material was the much

more accessible hydrocarbon fluorene; also the absence of 'quinone' formation in the oxidation, such as is observed with fluoranthene, renders the fluorenone-1-carboxylic acid in a high state of purity.

The loss of material and the time required in preparing the intermediates from fluorene offset this benefit to a considerable extent. Actually the relative yield of the acid from fluoranthene was greater than that from the same quantity of fluorene originally used, although the final oxidation gave a better yield from the hydrofluoranthene than from fluoranthene itself. (65%:50%.)

It was decided to continue the investigation further and prepare a series of fluorene-1-carboxylic acids, with a view to subsequent attempts to synthesise fluoranthene derivatives.

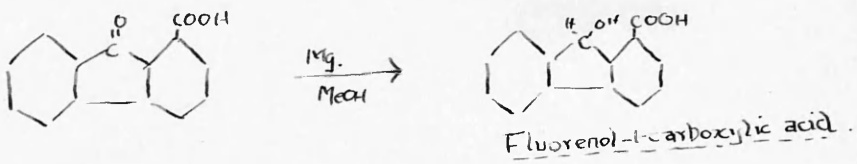
Reduction of fluorenone-1-carboxylic acid to fluorene-1-carboxylic acid (in 84% yield) has been described, using sodium amalgam as the reducing agent (xxv); the time required is about five hours.



Fluorene-1-carboxylic acid.

It was found that a modified Clemmensen reduction, using a hydrochloric-acetic acid medium required one hour only to prepare the desired product (in 95%-100% yield).

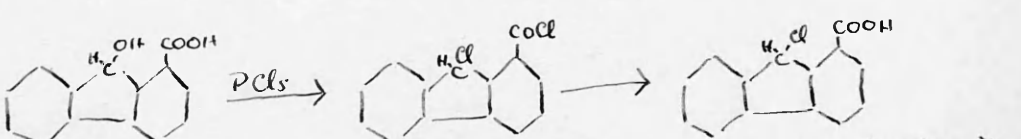
Reduction of fluorenone-1-carboxylic acid with the magnesium-methyl alcohol reagent produced the hitherto unknown 9-fluorenol-1-carboxylic acid (80%-85%):



Fluorenol-1-carboxylic acid.

(A great sensitivity of this reaction to impurities in the keto-acid or methyl alcohol was observed.)

Treatment of this acid with phosphorus pentachloride in chloroform yielded 9-chlorofluorene-1-carboxylic acid chloride, which hydrolised easily to 9-chlorofluorene-1-carboxylic acid (methyl ester m.p. 90°C.) :

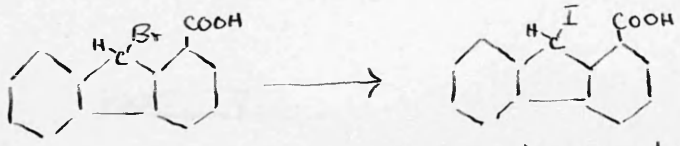


9-Chlorofluorene-1-carboxylic acid.

Hydrobromic acid in acetic acid converted the fluorenol-1-carboxylic acid to 9-bromofluorene-1-carboxylic acid (methyl ester m.p. 103°C.,amide m.p. 248°C.) (xxvi).

9-Bromofluorene-1-carboxylic acid

To complete the series 9-halogen-fluorene-1-carboxylic acids, 9-iodofluorene1-carboxylic acid was obtained by the action of sodium iodide in acetone on the corresponding 9-bromo-acid mentioned above.(xxvii)



9-Iodofluorene-1-carboxylic acid.

PART VII.

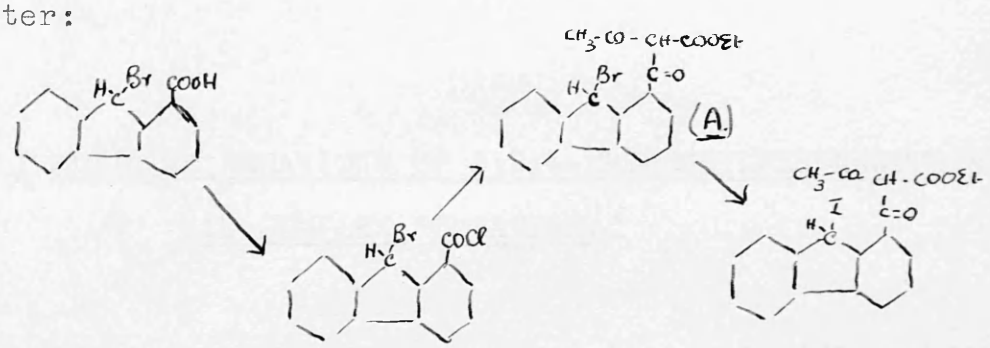
MISCELLANEOUS EXPERIMENTS: (1) SYNTHETIC APPROACHES TO THE METHYLFLUORANTHENES, AND (2) THE PECULIAR BEHAVIOUR OF METHYLFLUORANTHENES IN COMPLEX FORMATION.

MISCELLANEOUS EXPERIMENTS.

(i) SYNTHETIC APPROACHES TO THE METHYLFLUORANTHENES.

The following substances were prepared with a view to investigating possible syntheses of the methyl-fluoranthenes.

9-Bromofluorene-1-carboxylic acid chloride, obtained from the acid by the action of phosphorus pentachloride in chloroform, was condensed with sodium acetoacetic ester:



The 1-(9-bromo) fluorenoylacetoacetic ester (A) so obtained was converted into the corresponding 9-iodo-compound by sodium iodide in acetone.

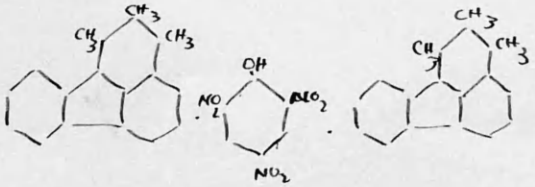
It was intended to test the reactivity of the halogen atom with regard to sensitivity towards the Reformatsky reaction (intramolecular).

Preliminary experiments in dry benzene gave indication that such a reaction was possible with this substance.

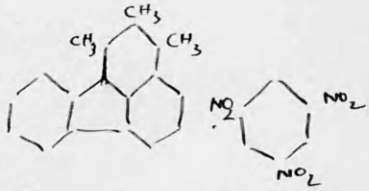
These experiments were originally postponed owing to the lack of material, and subsequently discontinued on the discovery of a more convenient synthetic method.

(ii) PECULIAR BEHAVIOUR OF 2:3:4-TRIMETHYLFLUORANTHENE IN COMPLEX FORMATION.

The curious behaviour of 2:3:4-trimethylfluoranthene in complex formation was observed. The hydrocarbon associated with picric acid in the ratio of one molecule of picric acid to two molecules of 2:3:4-trimethyl-fluoranthene, while with s-trinitrobenzene a normal 1:1 complex was formed.



'Picrate'



's-Trinitrobenzoate'

Unsuccessful attempts were made using various solvents to produce either the 1:1 picrate or the 1:2 trinitrobenzoate.

N.B. 2:4-Dimethylfluoranthene behaved normally in complex formation.

It was observed that fluorene exhibited a similar tendency to form complexes of varying ratio with different reagents (xxviii). It is not known whether the fluorene nucleus in the 2:3:4-trimethylfluoranthene is responsible for this curious behaviour.

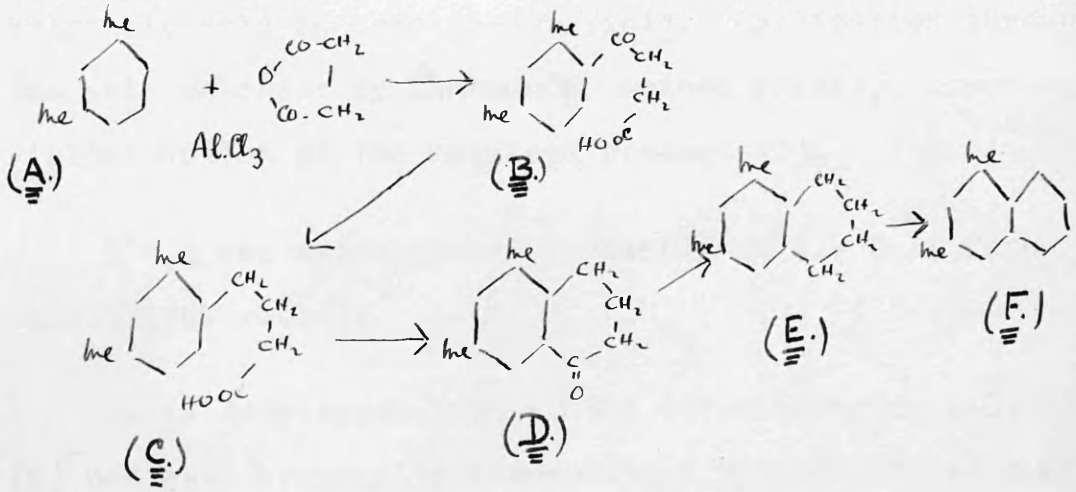
PART VIII.

IMPROVED SYNTHESIS OF 1:3-DIMETHYLNAPHTHALENE.

IMPROVED SYNTHESIS OF 1:3-DIMETHYLNAPHTHALENE

A considerable quantity of 1:3-dimethylnaphthalene was required as a starting material for the synthesis of 2:4-dimethylfluoranthene; accordingly, some investigation was made into the existing methods of preparation of the methylnaphthalenes (xxix, & xxx) in order to discover the most practicable means of obtaining 1:3-dimethylnaphthalene in quantity.

The method of Barnett and Sanders (xxxi) was chosen as the basic method of synthesis.



Various improvements were made on the original

synthesis. (A-F).

For the condensation of A to B chlorobenzene was used as a solvent for the reaction in place of the tetrachloroethane originally used; the yield of β-xyloylpropionic acid (B) obtained was almost theoretical.

The Clemmensen reduction of B to γ-xylylbutyric acid (C) was modified by the use of 4:1 concentrated hydrochloric acid-glacial acetic acid mixture, and 10 mols. at least of crude, lightly amalgamated zinc. The reduction by thid method was complete in two hours.

Ring-closure of the acid (C) to 5:7-dimethyl-α-tetralone (D) had originally been carried out by 80% sulphuric acid in some 25-30% yield. Cyclisation through the acid chloride by Bachman's method (xxxii), however, yielded 65-70% of the required product (D).

D - E was accomplished similarly to B - C in five hours. (70% yield).

Final dehydrogenation of the 5:7-dimethyltetralin (E) had been originally accomplished by selenium at 320°C. in about thirty hours time. It was found that the reaction could be carried out with sulphur at 220°C.(xxxiii) in about one hour. (This temperature could not be

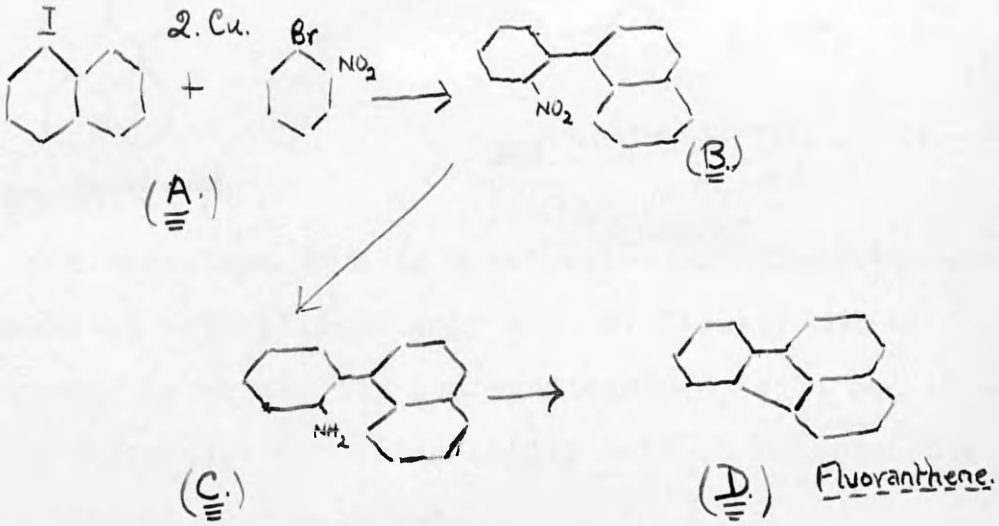
exceeded without risk of side-reactions). An 85-90% yield of 1:3-dimethylnaphthalene (E) was obtained.

About 35-40 g. of 1:3-dimethylnaphthalene were thus prepared.

PART IX.

SYNTHESIS OF FLUORANTHENE.

SYNTHESIS OF FLUORANTHENE.



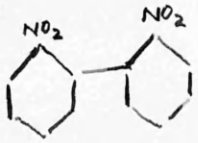
This synthesis (A-D) of fluoranthene was carried out to test the method for the more important synthesis of 2:4-dimethylfluoranthene.

α-Iodonaphthalene (A) was condensed with o'-nitrobromobenzene in the presence of copper bronze to give α-(o'-nitro)phenylnaphthalene (B).

Apparently o'-nitrobromobenzene was the only o'-nitrohalogen benzene which would yield the desired product with α-iodonaphthalene, as o'-chloronitrobenzene gave α:α'-dinaphthyl as the only isolatable product, and o'-iodonitrobenzene yielded uncrystallisable oils only.

(Probably a mixture of α-(o'-nitro)phenylnaphthalene and 2:2'-dinitro-diphenyl.)

α:α'-Dinaphthyl.



2:2'-Dinitrodiphenyl.

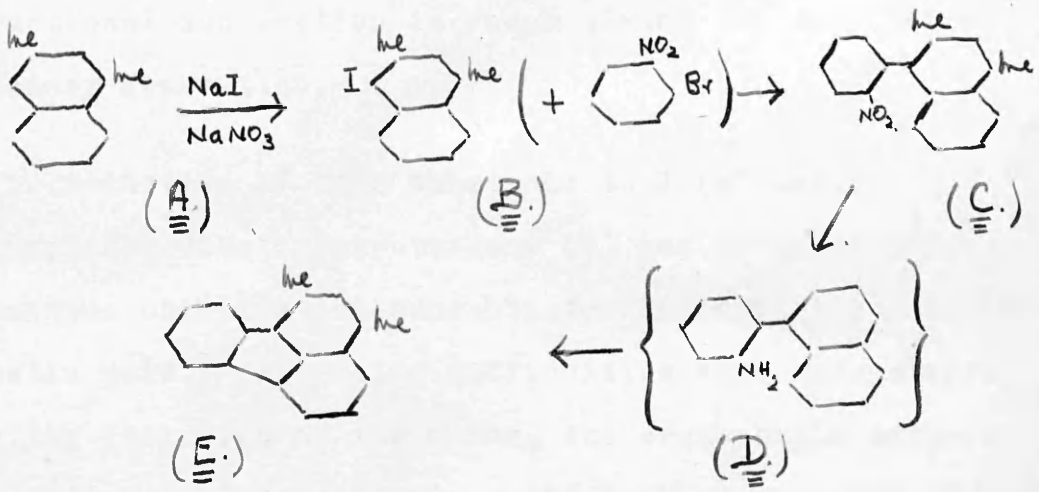
The reduction of B to α-(o'-amino)phenylnaphthalene (C) could be accomplished only with difficulty and in poor yields by either tin and hydrochloric acid, or stannous chloride in boiling acetic acid in the presence of dry hydrochloric acid gas.

Diazotisation and ring closure of the amine to fluoranthene (D) was carried out by Pschorr's method(xxxiv) i.e. the effect of copper bronze on the diazonium sulphate. The isolation of the fluoranthene was best accomplished by fractional vacuum sublimation of the oily reaction product.

PART IX A.

SYNTHESIS OF 2:4-DIMETHYLFLUORANTHENE.

SYNTHESIS OF 2:4-DIMETHYLFLUORANTHENE.



The 1:3-dimethylnaphthalene (A) required for the synthesis was prepared by the method described in Part VIII.

Iodination of the hydrocarbon was carried out by sodium or potassium iodide and sodium or potassium nitrate in glacial acetic acid. This was found to be the best method for iodination, as the method of Datta and Chatterjee (xxxv) yielded considerable by-products.

The product 1-iodo-2:4-dimethylnaphthalene (B) was condensed with o'-nitrobromobenzene in the presence of copper bronze in a similar manner to that condensation in the synthesis of fluoranthene, to yield 1-(o'-nitro)-phenyl-2:4-dimethylnaphthalene (C).

Considerable difficulty was encountered in the isolation of this substance from the oily reaction product, fractional sublimation in vacuo giving the only satisfactory separation.

Reduction of this substance to 1-(o'-amino)-phenyl-2:4-dimethylnaphthalene (D) was accomplished by stannous chloride and concentrated hydrochloric acid in acetic acid. As similar difficulties were encountered in the isolation of the amine, the crude basic material was diazotised directly to avoid loss of material through purification.

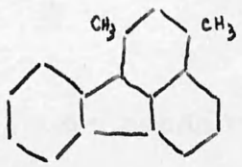
The diazotisation and ring closure to 2:4-dimethyl-naphthalene (E) was carried out in a similar manner to that described in Part IX.

The product obtained, after vacuum sublimation and crystallisation, did not show any depression of the melting point when mixed with the alleged 2:4-dimethyl-fluoranthene prepared as in Part III.

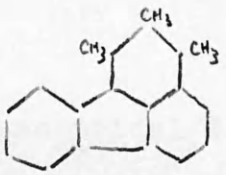
PART X.

THE CHEMISTRY OF 2:4-DIMETHYLFLUORANTHENE AND ITS BEARING ON THE CHEMISTRY OF FLUORANTHENE.

THE CHEMISTRY OF 2:4-DIMETHYLFLUORANTHENE (AND 2:3:4-TRIMETHYLFLUORANTHENE.)



2:4- Dimethylfluoranthene.

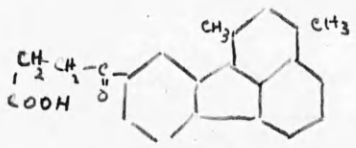


2:3:4- Trimethylfluoranthene.

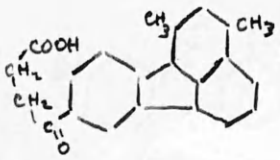
With the object of studying the effect of the two methyl groups of dimethylfluoranthene on the fluoranthene nucleus, a few simple derivatives were made by direct substitution under conditions similar to those used in the preparation of the corresponding fluoranthene derivatives (xxxvi).

Mononitration and bromination yielded as expected the single substances x-nitro- and x-bromo-, -2:4-dimethyl fluoranthenes respectively. It was originally thought that these derivatives must be 2:4-dimethyl-5-subst.-fluoranthenes.

Condensation of succinic anhydride (xxxvii) with 2:4-dimethylfluoranthene, however, produced a single substance instead of the expected two isomers A and B,



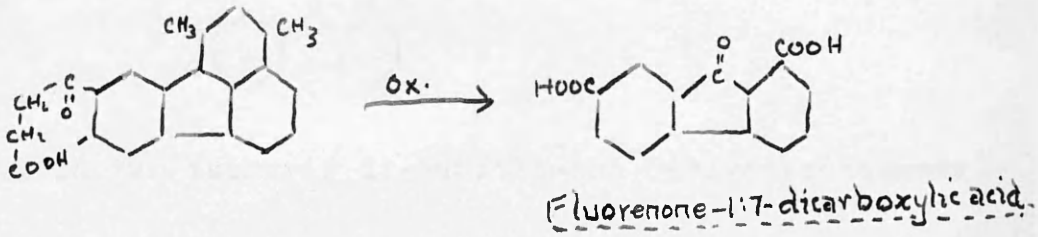
A.



B.

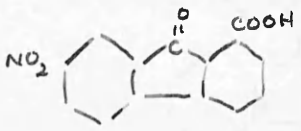
which would be produced by an unsymmetrical fluoranthene molecule substituting in position 11- or 12-.

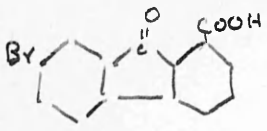
Oxidation of this acid (x-(2:4-dimethyl-) fluoranthenoyl-propionic acid) yielded fluorenone-1:7-dicarboxylic acid only. (Di-ethyl ester m.p. 114°C.) ([redacted])



This proved the substance to be a 12-substituted 2:4-dimethylfluoranthene.

Oxidation of the nitro-, and bromo-, -2:4-dimethyl-fluoranthenes produced, instead of the expected 2-nitro- and 2-bromo- fluorenone-1-carboxylic acids, x-nitro- and x-bromo- fluorenone-1-carboxylic acids, which were probably the hitherto unknown 7-nitro- and 7-bromo- fluorenone-1-carboxylic acids:

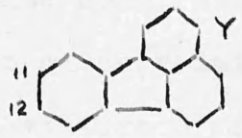




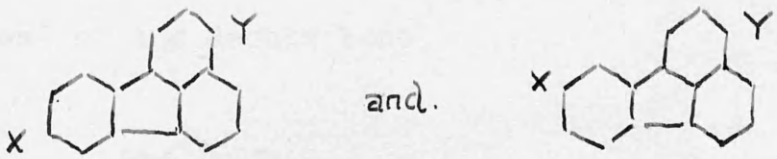
7-Nitro-, and 7-Bromo-, -fluorenone-1-carboxylic acids.

These facts apparently point to the theory that the 12- position instead of the expected 5- position is the most reactive position in 2:4-dimethylfluoranthene.

It is also observed that the 11- and 12- positions have <u>not</u> the equivalent reactivity as in fluoranthene itself, a mono- substituted derivative of which



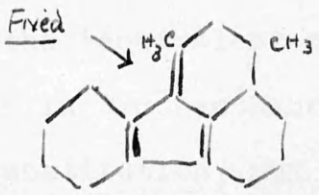
would yield two isomeric di-substituted derivatives ([redacted]):



Whereas single substances only were obtained from 2:4-dimethylfluoranthene.

The only feasible explanation of this * must be that a fixed double bond due to the 2- methyl group must exist between the 14' and 1' positions of the molecule.

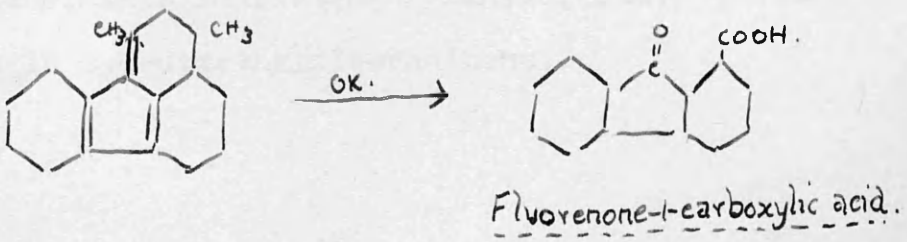
* Fixed (?) double bonds due to methyl groups (xxvii)



Thus the molecule is forced to act, not as fluoranthene but as a fluorene.

The fact that the 12' position is more equivalent to the reactive 7' position of the fluorene nucleus may be taken as a confirmatory support of this.

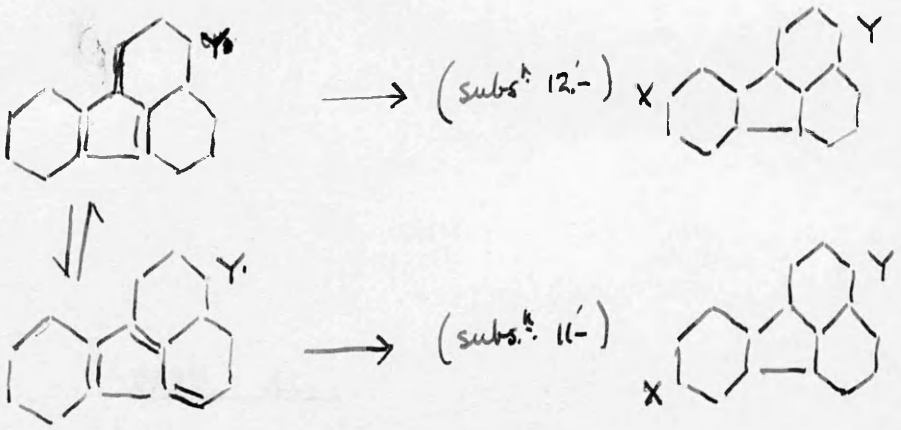
More definite confirmation is, however, obtained from the product of degradative oxidation which, instead of the expected mixture of fluorenone-1-carboxylic, and a fluorenone-tricarboxylic acids, is solely fluorenone-1-carboxylic acid, thus giving strong indication of the 'fixation' of the double bond.



Fluorenone-1-carboxylic acid.

There is, unfortunately, insufficient evidence to support the theory which may be derived from the above-

namely, that the 'equivalent reactivity' of the 11'- and 12'- positions in fluoranthene itself, (as shown by the isomeric di-substitution) may be due to the 'mobility' of the fluorene nucleus in fluoranthene:-



Note. A condensation of 2:3:4-trimethylfluoranthene similarly yielded a single mono-substituted 2:3:4-trimethylfluoranthene, thus indicating a similar state to that described in 2:4-dimethylfluoranthene.

PART XI.

C O N C L U S I O N.

CONCLUSION.

The research on the condensation of fluorene with acetone and the structures of the substances derived from the product of that condensation can now be considered completed.

Two new methods of obtaining fluoranthene derivatives have been discovered in the course of this work.

Firstly, there is the preparation of methyl-fluoranthenes and -hydrofluoranthenes by the ring-closure etc. of the product of condensation. This method is by far the most satisfactory synthetic means of obtaining fluoranthene derivatives yet known, as these substances may be obtained by this method easily and in whatever quantity desired. Theoretically the synthesis may be considered a modification of the original synthesis of fluoranthene by v. Braun and Anton (viii).

The other synthetic method described is unlikely to find application in any field other than the above, because of its unsuitability with regard to preparative work.

The 2:2:4-trimethyl-1:2-dihydro-, 2:2:4-trimethyl-1:2:3:4-tetrahydro, 2:4-dimethyl-, and 2:3:4-trimethyl-fluoranthenes described in this thesis are being tested

at present for carcinogenic properties.

The Chemistry of 2:4-dimethylfluoranthene has shown several points of interest. Much remains to be done, however, on that subject, both on that hydrocarbon and on the others, before any definite views can be expressed with regards to their properties and the possible light they may throw on the Chemistry of fluoranthene.

PART XII.

E X P E R I M E N T A L .

EXPERIMENTAL.

Oxidation of the ketonic acid $C_{19}H_{18}O_3$.

The ketonic acid (.5 g.) was gently boiled for four hours in glacial acetic acid (30 cc) with powdered sodium dichromate (3.5 g.), poured into dilute hydrochloric acid, and extracted with chloroform. The washed chloroformic layer was extracted with dilute caustic alkali and the brown-yellow caustic extract acidified with concentrated hydrochloric acid. The pink fluorenone-1-carboxylic acid precipitated was crystallisable from acetic acid. (Yield: .4 g.; 86%.)

Oxidation of 2:2:4-trimethyl-1:2-dihydrofluoranthene($C_{19}H_{18}$)

$C_{19}H_{18}$ (1 g.) in glacial acetic acid (45 cc), and powdered sodium dichromate (7 g.) were gently boiled for four hours and extracted as above. (Yield: .67 g.; 65%.)

Oxidation of 2:2:4-trimethyl-1:2:3:4-tetrahydrfluoranthene. $C_{19}H_{20}$

A similar oxidation of $C_{19}H_{20}$ yielded 50% of fluorenone-1-carboxylic acid.

Oxidation of $C_{16}H_{14}$ (?).

A similar oxidation of $C_{16}H_{14}$ (?) yielded 50% of fluorenone-1-carboxylic acid.

Oxidation of x-nitro-$C_{19}H_{20}O$. (Nitro-ketone.)

x-Nitro-$C_{19}H_{20}O$ on a similar oxidation to those previously reported, yielded 2-nitrofluorenone on evaporation of the chloroform extract of the reaction product. (Yield: 60%.)

Fluorenone-1-carboxylic acid from Fluorene.

Fluorene (100 g.) was condensed with acetone in the presence of caustic potash as described in J.C.S. and the oil obtained washed thoroughly with 65% sulphuric acid, extracted with ether, washed, etc., and the residue on removal of etherial solvent dissolved in glacial acetic acid (400 cc.). This solution was saturated with dry hydrobromic acid gas in vigorous steam for six hours. A considerable quantity of white crystals were precipitated. The solution was left overnight at 0°C., the white crystalline substance was then filtered, washed with acetic acid, and heated for one hour at 120°C. in a current of

air. Glacial acetic acid (700 cc) was added to the residue, sodium dichromate (350 g.) carefully inserted, andthe whole gently boiled for six to eight hours. The fluorenone-1-carboxylic acid was isolated as previously described. (Yield: 30 g.; 20%.)

Improved preparation of 2:2:4-trimethyl-1:2:3:4-tetrahydrofluoranthene. ($C_{19}H_{20}$).

The ketone $C_{19}H_{20}O$ (25 g.) in glacial acetic (300 cc) and hydriodic acid (s.g. 1.7; 60 cc) were boiled for five hours. The liquor was then poured into sulphurous acid solution and the solid which separated crystallised from methyl alcohol. (Yield: 12 g.; 55%.) {from previous method yield: 25%.}

Improved extraction of $C_{16}H_{14}$ (?) from the reaction mass.

The crude aqueous oil obtained by the action of water on the reaction mass after fusion of the ketone $C_{19}H_{20}O$ with phosphorus pentoxide at 250°C. was extracted with chloroform. After washing and drying the chloroform was distilled off and the residue dissolved in the minimum of glacial acetic acid. Excess picric acid dissolved in glacial acetic acid was added to this solution from which

the red picrate of $C_{16}H_{14}$ (?) was immediately precipitated. The hydrocarbon was recovered from the picrate in the usual manner.

The action of hydriodic acid on $C_{19}H_{19}Cl$.

$C_{19}H_{19}Cl$ (1 g.) and hydriodic acid (s.g. 1.7; 5 cc) were boiled for four hours in glacial acetic acid (300 cc). The product, m.p. 103°C., was extracted as in the preparation of 2:2:4-trimethyl-1:2:3:4-tetrahydrofluoranthene ($C_{19}H_{20}$) and proved to be identical with that substance.

The action of phosphorus pentoxide on $C_{19}H_{19}Cl$.

$C_{19}H_{19}Cl$ (2 g.) and phosphorus pentoxide (5 g.) were heated at 250°C. for two hours. The $C_{16}H_{14}$(?) produced was isolated (as described) by means of its picrate.

The action of phosphorus pentoxide on 2:2:4-trimethyl-1:2-dihydrofluoranthene. ($C_{19}H_{18}$).

A similar reaction to the above with $C_{19}H_{18}$ also yielded $C_{16}H_{14}$(?) which was isolated in the usual manner.

The action of zinc chloride on $C_{19}H_{18}$.

$C_{19}H_{18}$ (5 g.) and zinc chloride (10 g.) were heated at 250°C. for four hours. The $C_{16}H_{14}$(?) and $C_{19}H_{20}$ produced were isolated from the reaction mass as described in a similar reaction in J.C.S., 1937, 1739.

($C_{18}H_{14}$.) 2:4-Dimethylfluoranthene.

(1). 2:2:4-Trimethyl-1:2-dihydrofluoranthene (2 g.), was mixed with powdered selenium (.7 g.) and heated for five hours at 300°C. The mass was extracted with boiling acetic acid from which 2:4-dimethylfluoranthene separated on cooling. Recrystallised from alcohol, yellow rods, m.p. 113°-115°C. (Yield: 1.6 g.; 80%.)

(2). 2:2:4-Trimethyl-1:2:3:4-tetrahydrofluoranthene (2g.) was mixed with powdered selenium (1.3 g.) and treated as above. (Yield: 1.15 g.; 60%.)

Found:C,94.1%;H,6.26%; $C_{18}H_{14}$ requires:C,93.91%; H,6.09%.

Fluorene-1-carboxylic acid.

Fluorenone-1-carboxylic acid (5 g.), lightly amalgamated

granulated zinc (12 g.), in 50% glacial acetic acid-concentrated hydrochloric acid mixture (150 cc), and boiled vigorously for one hour. The solution became colourless. The solid precipitated on pouring the liquors into dilute acid, and was crystallised from acetic acid.
(Yield: 4.5 g.; 95%.)

Fluorenol-1-carboxylic acid.

Magnesium turnings (4 g.), and fluorenone-1-carboxylic acid (10 g.) were added to methyl alcohol (200 cc). Effervescence started immediately, and became violent as the reaction proceeded. When the reaction had ceased the mixture, now colourless, was poured into water and sufficient hydrochloric acid added to dissolve magnesium salts from the precipitate. The white solid residue was crystallised from methyl alcohol. (m.p. 195°C.; Yield:8.1g;80%).

Found:C,74.4%;H,4.6%; $C_{14}H_{10}O_3$ requires:C,74.3%;H,4.4%.

9-Bromofluorene-1-carboxylic acid.

Fluorenol-1-carboxylic acid (8 g.) was dissolved in warm glacial acetic acid (45 cc) and dry hydrobromic acid

gas passed in. The mixture darkened and at the saturation point a crystalline solid was precipitated. The hydrobromic acid gas was passed through the solution for a further 15 minutes, then the solution was left to cool. The 9-bromofluorene-1-carboxylic acid deposited was recrystallised from acetic acid. (M.p. 242°C., yield: 8.7 g.; 85%.)

Found:C,58.2%;H,3.35%;Br,27.5%. $C_{14}H_9O_2Br$ requires: C,58.1%;H,3.1%;Br,27.6%.

9-Bromofluorene--1-carboxylic acid chloride.

9-Bromofluorene-1-carboxylic acid (10 g.) was covered by dry chloroform (60 cc) and excess phosphorus pentachloride added (10 g.). The solution was boiled till all the acid had dissolved, and very little hydrochloric acid gas was emitted. The liquor was then decanted while hot from the excess phosphorus pentachloride, and the acid chloride precipitated by adding an equal volume of ligroin. Recrystallised from benzene. (M.p. 169°-72°C.) (Yield: 8.3 g.; 85%.)

Found:C,54.7%;H,2.7%;(Cl+Br),37.6%. $C_{14}H_8OBrCl$ requires: C,54.6%;H,2.6%;(Cl+Br),37.5%.

9-Bromofluorene-1-carboxylic acid methyl ester.

The acid chloride (2 g.) was boiled with methyl alcohol (15 cc) till all had dissolved. Long needles of the ester separated on cooling. (M.p. 102°-104°C.) (Yield: 1.9 g.; 97%.)

Found:C,59.6%;H,3.8%;Br,26.5%. $C_{15}H_{11}O_2Br$ requires: C,59.4%;H,3.6%;Br,26.4%.

9-Bromofluorene-1-carboxylic acid amide.

The acid chloride (2 g.) was shaken with ammonia (s.g. .88; 30 cc) for half-an-hour, and the amorphous solid washed and crystallised from acetic acid.(M.p.238°C.) (Yield: 1.9 g.; 98%.)

Found:C,58.6%;H,3.7%;Br,27.6%;N,5.0. $C_{14}H_{10}ONBr$ requires: C,58.4%;H,3.5%;Br,27.8%;N,4.9%.

1-(9-Bromo)fluorenoylacetoacetic ester.

9-Bromofluorene-1-carboxylic acid chloride (powdered) (6 g.) in dry ether (50 cc) was added to sodium aceto-acetic ester (6.1 g.) suspended in dry ether (50 cc).

The solution was boiled for three hours. The insoluble white residue was dissolved in water, and the aqueous solution acidified with very dilute acetic acid. The oil precipitated was extracted with ether, and immediately washed with water to remove any traces of excess acetic acid. The residue on removal of ether was recrystallised from methyl alcohol containing 2-3 drops of dioxan. The original etherial liquors were found (on evaporation) to contain more of the same product. (White prisms, m.p. 128°-30°C.) (Yield: 5.8 g.; 75%.)

Found: C, 59.7%; H, 4.2%; Br, 20.1%. $C_{20}H_{17}O_4Br$ requires: C, 59.9%; H, 4.2%; Br, 20.0%.

1-(9-Iodo)fluorenoylacetoacetic ester.

The above product (5 g.) in acetone (40 cc) was mixed with a solution of sodium iodide (1.88 g.) in acetone (50 cc). Almost immediately sodium bromide was precipitated. After standing one hour the solution was filtered, the acetone removed under reduced pressure, and the residue crystallised from methyl alcohol. Yellow prisms, m.p. 112°-114°C. (Yield: 5.3 g.; 95%.)
(Owing to a certain amount of decomposition on crystallisation, an analytically pure sample was not obtained.)

9-Chlorofluorene-1-carboxylic acid chloride.

Fluorenol-1-carboxylic acid (5 g.) was treated as in the preparation of 9-bromofluorene-1-carboxylic acid chlorid (pp. 70). Recrystallised from benzene.
White needles, m.p. 158°-160°C.

Found:C,63.8%;H,3.03%. $C_{14}H_8OCl_2$ requires:C,63.85%;H,3.04%.

9-Clorofluorene-1-carboxylic acid.

The acid chloride (2 g.) was boiled for ten minutes with acetic acid (40 cc). On cooling, needles of the acid separated. M.p. 226°-229°C (dec.). (Yield: Theoretical.)

Found:C,68.5%;H,3.63%. $C_{14}H_9O_2Cl$ requires:C,68.7%;H,3.68%.

9-Chlorofluorene-1-carboxylic acid methyl ester.

The acid chloride (2 g.) was boiled with methyl alcohol till all had dissolved. On cooling, long needles of the ester separated. M.p. 89°-92°C. (Yield: Theoretical.)

Found:C,69.5%;H,4.05%. $C_{15}H_{11}O_2Cl$ requires:C,69.7%;H,4.25%.

9-Iodofluorene-1-carboxylic acid.

9-Bromofluorene-1-carboxylic acid (2 g.) in acetone (25 cc) was added to the theoretical quantity of sodium iodide dissolved in acetone. Sodium bromide was immediately precipitated. After filtration and removal of solvent acetone in vacuo, the yellow residue was crystallised from acetone. Yellow needles, m.p. 183°.
(Yield: 1.8 g.; 80%.)

Found: I,37.6%. $C_{14}H_9O_2I$ requires: I,37.7%.

Picrate of 2:4-Dimethylfluoranthene.

Equimolar quantities of the hydrocarbon were dissolved in the minimum of boiling absolute alcohol. Fine orange-red needles of the picrate separated on cooling. M.p.206°C.

Found:C,62.9%;H,3.9%;N,9.0%. $C_{24}H_{17}O_7N_3$ requires:
C,62.7%;H,3.7%;N,9.1%.

s-Trinitrobenzene Complex with 2:4-Dimethylfluoranthene.

Equimolar quantities of s-trinitrobenzene and 2:4-dimethylfluoranthene were treated as above. Fine yellow needles. M.p. 223°C.

Found:C,65.0%;H,3.8%;N,9.5%. $C_{24}H_{17}O_6N_3$ requires:
C,65.0%;H,3.8%;N,9.5%.

Picrate of 2:3:4-Trimethylfluoranthene.

2 mols. of the hydrocarbon to 1 mol. of picric acid were dissolved in boiling absolute alcohol containing some drops of dioxan. Crimson needles of the picrate separated on cooling. M.p. 208°C.

Found:C,73.6%;H,5.9%;N,5.9%. $C_{25}H_{19}O_7N_3$ requires:
C,73.6%;H,5.9%;N,5.9%.

s-Trinitrobenzene Complex with 2:3:4-Trimethylfluoranthne.

Equimolar quantities of the hydrocarbon and s-trinitrobenzene were treated as above. Fine yellow needles, m.p. 229°C.

Found:C,65.8%;H,4.3%;N,9.2%. $C_{25}H_{19}O_6N_3$ requires:
C,65.6%;H,4.2%;N,9.2%.

β-Xyloyl(2:4)-propionic acid.

Anhydrous aluminium chloride (60 g.) was added to a

solution of m-xylene (20 g.) in chlorobenzene (100 cc) containing a suspension of succinic anhydride (20 g.). Evolution of hydrochloric acid fumes was immediately observed. The mixture was thoroughly shaken, allowed to stand overnight, and the acidic product worked up in the usual way. White needles (from ligroin). M.p. 114°C. (Yield: 37 g.; 95%.)

γ-Xylyl(2:4)-n-butyric acid.

To the above acid (20 g.) suspended in 250 cc. of 3:1 concentrated hydrochloric acid-glacial acetic acid mixture were added lightly amalgamated granulated zinc (50 g.). The whole was vigorously boiled for two hours (frothing was observed). The reduced acid was extracted in the usual manner. Crystallisation from ligroin yielded white needles, m.p. 78°C. (Yield: 14g.; 75%.)

5:7-Dimethyltetralone.

γ-Xylyl(2:4)-n-butyric acid (20 g.) in dry benzene (100 cc) was boiled with phosphorus pentachloride (20 g.) for two hours. The benzene and phosphorus oxychloride

were then removed under reduced pressure and the residue dissolved in dry benzene (100 cc). To this solution was added anhydrous aluminium chloride (25 g.) and the whole heated at 35°C. for four hours. The product was isolated as described (xxxi). (Yield: 11.5 g.; 65%.)
M.p. 50°C.

5:7-Dimethyltetralin.

5:7-Dimethyl-α-tetralone (20 g.) was reduced in a similar manner to the reduction of β-xyloyl(2:4)-propionic acid. B.p. c'a 130°C./12 mm.
(Yield: 12 g.; 70%.)

1:3-Dimethylnaphthalene.

5:7-Dimethyltetralin (10 g.) and sulphur (4 g.) were heated at 220°C. for one hour, then the product carefully distilled in vacuo from the reaction mixture. B.p. 130°C./10 mm. (Yield: 8.1 g.; 85%.)

α-(o'-Nitro)phenylnaphthalene.

α-Iodonaphthalene (7 g.), o'-bromonitrobenzene (6.0 g.), and copper bronze (5 g.) were heated at 240°-250°C. for

three hours. The mass was then extracted with dry ether. After removal of the etherial solvent the residue was crystallised from methyl alcohol. Yellow needles, m.p. 89°-90°C. (Yield: 4 g.; 60%.)

Found: C,77.0%; H,4.5%; N,5.8%. $C_{16}H_{11}O_2N$ requires: C,77.1%; H,4.4%; N,5.6%.

α-(o-Amino)phenylnaphthalene.

The nitro compound (3 g.) and stannous chloride (2 g.) were boiled in acetic acid solution (25 cc) while a steady stream of anhydrous hydrochloric acid gas was passed into the liquor for four hours. After extraction in the usual manner for amines, the compound was crystallised (with difficulty) from methyl alcohol. White needles, m.p. 61°-63°C. (Yield: Poor; 30%.)

Found: C,87.8%; H,6.0%; N,6.5%. $C_{16}H_{13}N$ requires: C,87.7%; H,5.9%; N,6.4%.

Fluoranthene (by Diazotisation etc. of Amine).

The amine (2 g.) was diazotised in 15% sulphuric acid (15 cc), copper bronze (.5 g.) added and the whole warmed till the diazonium solution turned milky. Heating was

continued for ten minutes, then the oil formed was extracted with chloroform, the extract washed etc., and the residue vacuum sublimed after removal of solvent. The first fraction (subliming at 130°-150°C./11mm) was crystallised from aqueous acetic acid. Lond needles of fluoranthene, m.p. 108°C. separated. (yield: .5 g.;30%.)

1-Iodo-2:4-dimethylnaphthalene.

2:4-Dimethylnaphthalene (5 g.), previously purified by means of its picrate, sodium iodide (4.8 g.), and sodium nitrate (3.5 g.) were boiled in acetic acid (200 cc) till the colour iodine produced when the acetic acid first boiled had disappeared (5-6 hours). The solution was then poured into water and extracted with chloroform. The extract (after washing etc,) was fractionally distilled under reduced pressure, the fraction b.p. 185°-95°C./11mm being retained. (Yield: 7.2 g.; 78%.)

1-(o-Nitro)phenyl-2:4-dimethylnaphthalene.

The iodohydrocarbon (5 g.), o-nitrobromobenzene (3.8g.) and copper bronze were thoroughly mixed and treated as in

the preparation of α-(o'-nitro)phenylnaphthalene. The residue after removal of etherial solvent is sublimed in a good vacuum. The fraction subliming at 180°-200°C./9mm (reddish glassy material) was scratched in methyl alcoholic suspension and a yellow solid obtained. Crystallised from methyl alcohol in yellow needles, m.p. 110°-12°C. (Yield: Poor, c'a0.5-1 g.)

Found:C,77.85%;H,5.3%. $C_{18}H_{15}O_2N$ requires:C,78.0%;H,5.4%.

2:4-Dimethylfluoranthene (Synthesis of-).

The nitro compound prepared in the previous paragraph (2 g.) was reduced as in the preparation of α-(o-amino) phenylnaphthalene and the basic material formed diazotised etc. similarly to the diazotisation of the above amine. Vacuum sublimation of the oil produced yielded (at 130°-140°C./11mm) a solid, m.p. 108°C. which did not depress the m.p. of the alleged 2:4-dimethylfluoranthene prepared as on page 68. (Yield: c'a0.01 g.)

x-Bromo-2:4-dimethylfluoranthene.

2:4-Dimethylfluoranthene (2 g.) in carbon disulphide (15 cc) were added to bromine (1.4 g.) in carbon disulphide

(15 cc) containing traces of phosphorus tribromide, and the whole boiled gently till the colour of the bromine had disappeared. The solvent was then removed under reduced pressure and the residue crystallised from absolute alcohol. (Discard oil first precipitated.) Small crystals, m.p. 118°-20°C. (Yield: 1.7 g.; 65%.)

Found:C,69.8%;H,4.2%. $C_{18}H_{13}Br$ requires:C,69.9%;H,4.2%.

x-Nitro-2:4-dimethylfluoranthene.

2:4-Dimethylfluoranthene (2 g.) in acetic acid (30 cc) was added to fuming nitric acid (s.g.1.5;0.7 cc) in acetic acid (10 cc) and the solution heated to the boiling point till the evolution of nitrous fumes ceased (about 5-10 minutes). On cooling the solution deposited a yellow oily solid which, on recrystallisation from acetic acid, (discard the first oily precipitate) yielded yellow needles m.p. 175°C. (Yield: 1.8 g.; 80%.)

Found:C,78.4%;H,4.55%. $C_{18}H_{13}O_2N$ requires:C,78.6%;H,4.7%.

12-(2:4-Dimethyl)fluoranthenoyl-β-propionic acid.

Dimethylfluoranthene (2 g.) dissolved in chloro-

benzene (20 cc) containing suspended succinic anhydride (0.75 g.) was warmed to 30°C. for two hours after addition of anhydrous aluminium chloride (3.5 g.). The mass was left overnight, then the acid extracted in the usual manner. Small yellow-green prisms from acetic acid, m.p. 218°C. (Yield: 2.1 g.; 72%.)

Found: C, 80.00%; H, 5.43%. $C_{22}H_{18}O_3$ requires: C, 80.00%; H, 5.45%.

x-(2:3:4-Trimethyl)fluoranthenoyl-β-propionic acid.

A similar experiment to the previous preparation yielded c'a 60% of the acid, m.p. 212°C.

Found: C, 80.39%; H, 5.86%; $C_{23}H_{20}O_3$ requires: C, 80.23%; H, 5.81%.

Oxidation of 12-(2:4-Dimethyl)fluoranthenoyl-β-propionic acid.

The acid (1 g.) in acetic acid (40 cc) was boiled for fou r hours with sodium dichromate (8 g.). The acid product obtained in the usual way was identified as fluorenone-1:7-dicarboxylic acid by its diethyl ester, m.p. 114°C.

Oxidation of x-Bromo-2:4-dimethylfluoranthene.

A similar oxidation of the above substance yielded a yellow crystalline acid which, on purification from acetic acid, melted at 236°C. It was not 2-bromo-fluorenone-1-carboxylic acid. (It was named x-bromo-fluorenone-1-carboxylic acid.)

Found:C,55.2%;H,5.43%. $C_{14}H_7O_3Br$ requires:
C,55.4%;H,5.45%.

Similarly, x-nitro-2:4-dimethylfluoranthene yielded x-nitrofluorenone-1-carboxylic acid, m.p. 245°C.